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Fabrication of Carbon Based Nano Composite for EMI Shielding Applications

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Abstract: The increased use of electronic devices around the world has made EMI a serious concern. Devices that are vulnerable to interference, such as computers, broadcasting receivers, navigation systems etc, must often be shielded to protect them from the effects of EMI. In this study, copper nanoparticles were synthesized through a relatively large-scale, high-throughput process, coated with protective shells of graphene in order to get a metal nanopowder of high air stability and chemical inertness. This method occurs through the chemical reduction of copper sulfate with sodium hypophosphite in ethylene glycol within the presence of a polymer surfactant (PVP), which was included to prevent aggregation and give dispersion stability to the resulting colloidal nanoparticles. Further obtained copper nanoparticles graphene nanocomposites. The high stability of graphene copper nanocomposite makes them economically a most attractive alternative to silver or gold nanoparticles, and will strongly facilitate the industrial use of metal nanoparticles in consumer goods.

Keywords: - Graphene, Cu Nanoparticles, Nanocomposites, EMI Shielding.

Introduction

Graphene

Carbon is one of the most abundantly found elements in the earth's crust. It has many allotropes and each of them has proved to be useful to the mankind. Graphene is one of these allotropes. It is a single atom-thick sheet of hexagonally arranged sp^2-bonded carbon atoms which is freely suspended or adhered on a foreign substrate. Its lateral dimensions may vary from several nanometers to micro scale. Monolayer is that the purest and is beneficial for high-frequency physics. Bi-layer and tri-layer Graphene, two and three layers respectively, exhibit different properties with the increase in the number of layers. Due to these properties Graphene seems to have many applications in various sectors [1, 6].

Carbon based Nanocomposites

Graphene sheets, which have unique structure and fascinating properties, can be considered as promising nanoscale building blocks of new composites. We demonstrate how deposition of graphene layers on copper can be realized on a technical scale and enables full protection of the copper metal core up to 200°C under humid air. The protected copper can be used in electromagnetic interference shielding. We decided to investigate the potential use of most recently developed graphene copper nanocomposites as a potential substitute for the presently used noble metal nanocolloids[4,5].

EMI Shielding Effectiveness

EMI shielding refers to the reflection and/or adsorption of electromagnetic radiation by a material that acts as a shield against its penetration. As electromagnetic radiation, particularly at high frequencies (radio waves, such as those emanating from cellular phones) tend to interfere with electronics, EMI shielding of both electronics and radiation sources is needed, and is increasingly required by governments around the world. The importance of EMI shielding relates to high demand on the reliability of electronics, and the rapid growth of radio frequency radiation sources. EMI shielding is distinguished from magnetic shielding, which refers to the shielding of magnetic fields at low frequencies.

The EMI shielding effectiveness (SE) of a material is defined as the ratio between the incident power (P_i) and outgoing power of an electromagnetic wave (P_t). SE is expressed in decibels (dB) and is given by

$$SE\ (\text{dB}) = -10 \log (P_t/P_i)$$

When electromagnetic radiation is incident on a shielding material, phenomena such as reflection, absorption and multiple reflection occur. The total EMI SE (SE_{total}) is the summation of the SE due to absorption (SE_A), reflection (SE_R), and multiple reflection (SE_M), i.e.,

$$SE_{total} = SE_A + SE_R + SE_M$$

For single layer when SE_A is ≥ 10 dB, then $SE_M \rightarrow 0$ and can be neglected .

The transmittance *T* is measured from the ratio of *Pt* to

Pi, i.e.,

$$T = (Pt/Pi)$$

Thus, the SE_{total} of shielding material can be written as

$$SE_{total} = -10 \log T$$

In two port network S-parameter S_{11} (S_{22}), S_{21} (S_{12}) represents the reflection and the transmission coefficients

$$T = |E_T/E_I|^2 = |S_{21}|^2 \ (|S_{12}|^2)$$
$$R = |E_R/E_I|^2 = |S_{11}|^2 \ (|S_{22}|^2)$$
$$A = 1 - R - T$$

If absorption is calculated on the basis of EM wave inside the material after reflection i.e. 1-R Then effective absorbance, A_{eff} is defined as

$$A_{eff} = (1–R–T) / (1–R)$$

with respect to the power of the incident electromagnetic wave inside the shielding material, where R is the reflectance. Then SE due to reflectance and effective absorbance can be described as:

$$SE_R = -10 \log (1-R)$$
$$SE_A = -10 \log (1-A_{eff}) = -10 \log [T/(1-R)]$$

Experimental

Chemicals Used: Graphite powder, H_2SO_4, HNO_3, Hydrazine hydrate, Poly vinyl pyrrolidone (PVP, K-30), sodium hypophosphite ($NaH_2PO_2.H_2O$), copper sulfate ($CuSO_4.5H_2O$), ethylene glycol, acetone and distilled water etc.

Methodology

Synthesis of graphene by chemical route method:

Graphene were synthesized by the following procedure:

- Taken graphite fine powder (Loba chemie) of certain amount in a beaker of capacity 5 liter.
- Oxidized the above graphite powder with H_2SO_4 and HNO_3 mixed (in the ratio of 1:3) with the addition of small amount of distilled water and continuously stirred vigorously for 5 to 6 hours.
- Filtered and washed with distilled water many times to remove acids.
- Dry the materials at 120^{0}C for more for 3 hours.
- The product so formed is graphite oxide or activated graphite.
- Reduction of above material with Hydrazine Hydrate ($NH_2.NH_2.H_2O$), such that quantity of hydrazine should be 1/6 volume of graphite oxide.
- Again stirring vigorously for 10-12 hours.
- Ultrasonicated for 24 hours with a temperature of 60-70^{0}C.
- Washed with distilled water to remove impurities.
- Dried at 120^{0}C.
- The material so formed is graphene.

Incorporation of copper nanoparticles into graphene matrix:

Graphene coated copper nanoparticles were synthesized by the following procedure:

- 110gm PVP, 40gm sodium hypophosphite and 10gm graphene were mixed into 400ml ethylene glycol inside a round-bottom flask.
- Solution was vigorously stirring at room temperature under ambient atmosphere.
- The mixture was heated to 90^{0}C at a rate of 5^{0}C min^{-1}.
- 100ml of a 1 M solution of copper sulfate in ethylene glycol was prepared and heated at 90^{0}C.
- Copper Sulfate solution was then rapidly added into the PVP/sodium hypophosphite/graphene solution while stirring vigorously.
- Reduction occurred and the color of the suspension turned from green to reddish brown within 2–3 min, indicating the formation of copper nanoparticles.
- The reaction was quenched and the suspension was rapidly cooled by adding chilled deionized (DI) water.
- The copper nanoparticles have been separated and washed with DI water by using centrifugation, at the same time as the usage of acetone as a non-solvent, to remove extra PVP and side products.
- Reduction of above material with Hydrazine Hydrate ($NH_2.NH_2.H_2O$).
- The resulting precipitate was dried under vacuum at 40^{0}C for 2–3 h.
- The sample thus obtained was graphene copper nanocomposites.

Result & Discussion

Four Probe analysis

The samples graphene and graphene copper nanocomposite were pressed into pellets by applying a pressure between 7 to 10 tonnes by using a manual hydraulic press. These pellets were used for measuring the conductivities by four probe method. The values of conductivity of the synthesized graphene and graphene copper nanocomposites are given in table. The conductivity of graphene, graphene copper composites and graphene copper composites after annealing at 350^{0}C was found to be 3.118, 2.8736 and 1.678 S/cm. In principle, one would have observed a decrease in conductive behavior with increasing heating composites.

S.No.	Sample Name	Thickness (mm)	Resistance(Ω)	Conductivity (S/cm)
1	Graphene	1.80	3.3097	3.118
2	Cu-graphene	1.82	3.551	2.873
3	Cu-graphene 350^{0}C	1.35	8.1956	1.678

EMI shielding analysis

The enhanced electrical properties of the copper graphene composites prepared by the chemical reduction method show potential applications of the nanocomposites for electronics applications, such as EMI shielding and for electrostatic charge dissipation, anti-static charge dissipation applications

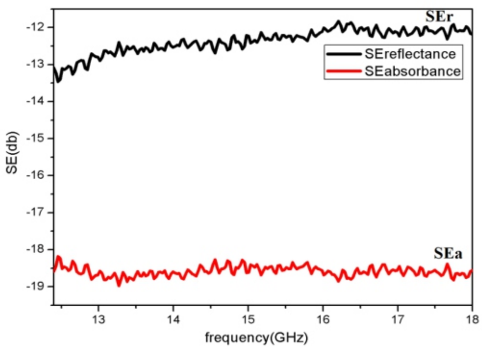

Fig.(a) **SE$_R$ and SE$_A$ of graphene coated copper nanoparticles as a function of frequency measured in the Ku-band.**

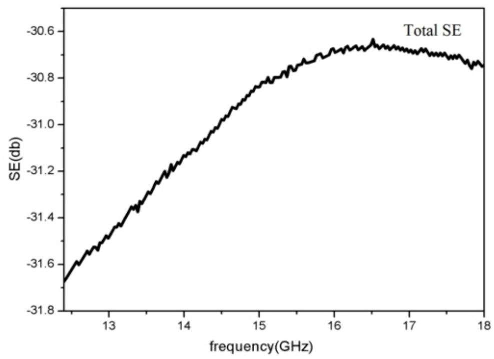

Fig.(b) SE **$_{Total}$ of graphene coated copper nanoparticles as a function of frequency measured in the Ku-band**

Microwave absorption is the technique by which the ability to absorb the electromagnetic radiations of microwave region (12-18 GHz) is calculated for the calculation of this property using Agilent technologies PNA Network Analyzer E 8362B. The thickness of sample was 2.87 mm. Preliminary results have indicated that the reflectance values of graphene copper composites lies in the range of 11.8 – 13.4 dB whereas absorbance values lies in the range of 18.2 dB to 18.9 dB here EMI shielding effectiveness of 31 dB was achieved in Ku-band (12-18 GHz).

The mechanism of EMI shielding was investigated by comparing the contribution of reflection and absorption to the total EMI shielding effectiveness. Figure (b) show the total EMI shielding effectiveness of copper graphene composite obtained by chemical reduction method. EMI SE up to 31 dB (30.6 – 31.6 dB range) in the frequency range 12-18 GHz was achieved. When the total EMI SE (SE$_{total}$) of copper graphene composite was further divided into the reflection and absorption components it was found that SE$_A$ was more than SE$_R$.

The primary mechanism of EMI shielding is usually reflection of the electromagnetic radiation incident on the shield which is a consequence of the interaction of EMI radiation with the free electrons on the surface of the shield. Thus the shield must be electrically conducting although a high conductivity isn't required. Absorption is usually a secondary mechanism of EMI shielding whereby electric dipoles in the shield interact with the electromagnetic fields in the radiation.

SE$_R$ of the composites is about 11.8–13.4dB. As long as the conductive component is uniformly and well dispersed in the graphene matrix, the shielding effectiveness proves in theory and in practice to be a function of conductivity and thickness.

Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) of graphene and graphene copper nanocomposites become completed under N_2 flow using Instrument TGA METTLER 851 and recorded graph between % weight loss Vs temperature .The samples were heated from room temperature to 800^{0}C at 15^{0}C/min. The results are shown in Figure. As expected, graphene and graphene copper composites were stable up to 500^{0}C and 550^{0}C respectively. On the other hand, graphene showed thermal stability due to the removal of oxygen-containing functional groups by hydrazine reduction. The degradation continues up to 800˚C.The total loss of graphene copper composites in the mass was 16.8

%.The TGA plot for the graphene, graphene copper composites show loss in mass started at 500˚C and 550˚C respectively. The degradation of the graphene, graphene copper nanocomposites and graphene copper nanocomposites after annealing 350˚C, continues up to 800˚C respectively along with total loss of 10.2%, 21.8 %, 16.8 %.

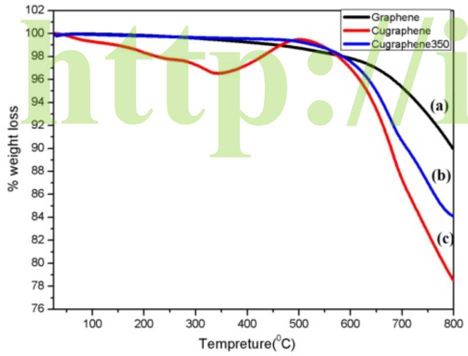

Fig. TGA Curve of graphene(a), copper graphene composites(c)and copper graphene composites after annealing at 350^{0}C(b).

Fourier Transform Infrared Spectroscopy analysis (FTIR)

Figure shows FTIR spectra of graphene, graphene copper nanocomposites and graphene copper nanocomposites after annealing 350^{0}C .The absence of different type of oxygen functionalities in graphene and graphene copper nanocomposites was confirmed at 1720 cm^{-1} (stretching vibrations from C=O), at 1600 cm^{-1} (skeletal vibrations from unoxidized graphene domains), at 1220 cm^{-1} (C-OH stretching vibrations), and at 1060 cm^{-1} (C-O stretching vibrations). FTIR peak of graphene presents that O-H stretching vibrations observed was significantly reduced due to deoxygenation.

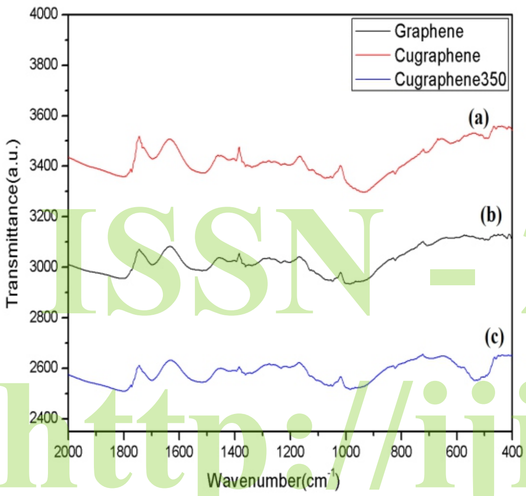

Figure: FTIR spectra of copper graphene composites (a), graphene(b), and copper graphene composites after annealing 350^{0}C(c).

Conclusions

Graphene copper nanocomposites within a more preferable size regime have been successfully fabricated by the chemical reduction method using sodium hypophosphite as a reducing agent and PVP as a stabilizing polymer.The recent addition approach and controlling of the lowering agent-to-copper precursor mole ratio used on this study are considered to have played vital roles inside the resulting formation of smaller and well-dispersed copper nanoparticles.

We have established that copper as a low-fee non-noble metallic can resist oxidation below ambient situations if coated by graphene. Graphene coatings offer an economically attractive route to the broader use of metal nanoparticles for ambient conditions. Our present example using copper as a substitute for silver or gold EMI shielding demonstrates a first step in the development of commodity metal nanoparticle applications. Controlling the oxidation and corrosion of the technically most important nonnoble metals through the managed deposition of graphene coatings will permit a much broader use of common transition organization metals in the form of nanomaterials.

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