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RESEARCH ARTICLE

Chemical synthesis of graphite nanoparticles and study of microwave radiation absorption by graphite nanocomposites

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Abstract

Nanostructured radar absorbing materials (RAMs) have received steadily growing interest because of their fascinating properties and various applications compared with the bulk or microsized counterparts. These nanostructured materials have increased surface area, number of dangling bond atoms and unsaturated co-ordination on surface lead to interface polarization, multiple scatter and absorbing more microwave. In this paper, new method was developed to produce graphite nanoparticles. Graphite powder is immersed in a mixed with solution of nitric and calcium citrate. After heating the solution up to 50°C and leaving them in the air for 12 hours in presence of low magnetic field, we obtained graphite nanoparticles. This process could provide an easy and inexpensive method for the preparation of graphite nanoparticles. They possess remarkable electrical, mechanical, optical, thermal and chemical properties and low cost material which make them a perfect fit for many engineering applications. Chemically synthesized graphite nanoparticles were mixed with barium sulphate to get graphite nanocomposite. These nanocomposite were used as microwave absorbent material to study the microwave properties like reflection coefficient and return loss. The results showed that these nanostructured composite can be used to design multilayer radar absorbing materials.

INTRODUCTION

Nanocrystals (NCs) or nanoparticle (NPs) have different physical and chemical properties from their bulk materials (Hodes 2007; El-Sayed 2004; Alivisatos 1997). They also have high surface to volume ratio which differs the characteristics of the nanocrystals or nanoparticles from the bulk materials(Goesmann and Feldmann 2007; Peng 2009). The unique properties of nanocrystals or nanoparticles can be utilized in the applications like optoelectronics, energy conversion, magnetic storage or nanomedicine (Talapin et al. 2010; Semonin et al. 2012; Lohse and Murphy 2012; Lee et al. 2007; Reddy et al. 2012; Wang et al. 2008; Bouzigues et al. 2011). Synthesis of NCs or NPs with different structures, compositions and sizes is achieved for many type of compounds like chalcogenides, transition metal oxides, lanthanide base compounds, actinides based compounds and noble metals(Kwon and Hyeon 2008; Park et al. 2007; Rao et al. 2007; Jun et al. 2006; Jun et al. 2005).

Radio absorbing materials (RAMs) have properties of absorbing microwave energy and reducing electromagnetic backscatter. They can be used in many applications like stealth technology of aircrafts, television image interference of high-rise buildings and microwave dark room and protection (Shin and Oh 1993; Peng et al. 2005). RAMs are designed to suppress the reflected electromagnetic energy incident on the surface of the absorber by dissipating the magnetic or electric fields of the wave into heat. Excellent RAMs exhibit properties like strong microwave absorption with a high magnetic and electric loss (Ruan et al. 2000; Babbar et al. 2000; Cho et al.). Nanostructured RAMs also exhibit strong microwave absorption. There are many types of nanostructured RAMs like nanocrystal RAMs, core-shell nanocomposite RAMs, nanocomposite of MWCNT and inorganic materials RAMs, nanocomposite of nanostructured carbon and polymer RAMs. These properties of nanoparticles (NPs) lead to interface polarization and multiple scatter, which is useful to absorb more microwave.

Graphite nanoparticles are the most researched materials due to its unique properties such as good electrical/thermal conductivity, enhanced chemical/bio compatibility high surface area, excellent dimensional stability, optical properties and corrosion resistance. Graphite nanoparticles have different properties from its raw material graphite. Hence they have been used in wide applications such as transistor, battery, supercapacitor, fuel cell, biosensor, composites, and so on (Zhang et al. 2006, ; Shenderova et al. 2002; Wang et al. 2002; Lu et al. 2009; Wisser 2006,).

In this paper, graphite nanoparticles are being synthesized in the laboratory using chemical reagent nitric acid (HNO_3) and calcium citrate under low magnetic field. Then graphite nanoparticles were used to make graphite nanocomposites. These nanocomposites were used to absorb microwave radiation. The analysis of crystallography and particle sizes of graphite nanoparticles was done by XRD and small angle X-ray scattering (SAXS) methods.

Methodology:

The starting materials for synthesis of graphite nanoparticles were graphite, calcium citrate and conc. nitric acid (HNO_3). First, 5.0g of graphite was slowly added to nitric acid (15mℓ) in a non magnetic cylindrical container .Citrate was slowly added to the solution in the presence of magnetic field of 10^{-2} to 10^{-3} Tesla and was then placed in the air for 12 hours at $50^{\circ}C$. Most graphite precipitated on the bottom but some reacted carbons were floating. . We separate out (by filtering) only the floating graphite which has reacted with the calcium citrate. The floating carbon materials were transferred into water, filtrated and dried. The filtered and dried sample obtained were graphite nanoparticles (Dai et al. 1999; Ago et al. 2002).

The graphite nanoparticles were mixed with barium sulphate and water to form paste. The paste was heated upto $45°C$ and then compressed by applying pressure of 5 MPa and again heated upto $145°C$. By applying heat and pressure, graphite nanoparticles and barium sulphate formed the graphite nanocomposite film of thickness 3mm as shown in figure 1. Microwave radiation absorption properties of graphite nanocomposite was tested by using microwave bench.

Interpretation of particle size by XRD analysis:

The graphite nanoparticles were studied using XRD (XRD-panalytical, operated at 40 kV and 30 mA, Cu-K∝). A series of intensive peaks (2θ/deg: 26.7, 42.6, 44.8, 54.7, 77.6, 83.7) corresponding to graphite lattice reflections of Cu-K∝ photons can be observed at figure 2. The particle/grain size of graphite nanoparticles were determined by the X-ray line broadening method using the Scherer equation(from the FWHM of the most intensive peak at $26.7°$) was found out to be about nm.(Cullity 1978):

Scherer equation

$$\beta = \frac{k\lambda}{D\cos\theta} + \varepsilon\tan\theta \tag{1}$$

where D is the crystallite size in nanometers, λ is the wavelength of the radiation (1.54056 Å for Cu-K∝ radiation), k is a constant equal to 0.94, β is the peak width at half maximum intensity, and θ is the peak position, ε is lattice strain.

Small angle X-ray scattering (SAXS) analysis:

SAXS is usually applied to tasks of determining spatial sizes for clusters, crystallites, powder and polycrystalline grains, layer thicknesses and superlattice periods. All these values are ranging in the order of magnitude from nanometers to hundreds of nanometers (Sharkov et al. 2013). The standard procedure of SAXS analysis includes data treatment in three different data ranges (Sharkov et al. 2013). The angular scale was transformed initially into the scale of wave vector magnitudes $q = 4\pi \sin \theta/\lambda$ (with θ being one half of the scattering angle). In the vicinity of the incident beam direction the SAXS curve was broadened; the FWHM (full width at half maximum) of this SAXS peak allowed one to estimate homogeneity sizes in the sample. SAXS data analysis has led to following results as shown in figure 3. Graphite nanoparticles have appeared to contain grains with particle sizes up to 10–40 nm.

Results for microwave absorption:

Study of microwave absorption by Graphite nanocomposite:

The test on graphite nanocomposite was carried out using microwave bench Klystron Test bench NV9000 and results of microwave absorption were shown in table 1.

VSWR vs Frequency

Measurements were carried out for graphite nanocomposite. The results of VSWR measurement for the both sample depending on the frequency are shown in figure 4 . The figure shows that the VSWR value depends on particle size of the material. As the particle size decreases VSWR decreases, which show that the value of refection from the surface of the material decreases.

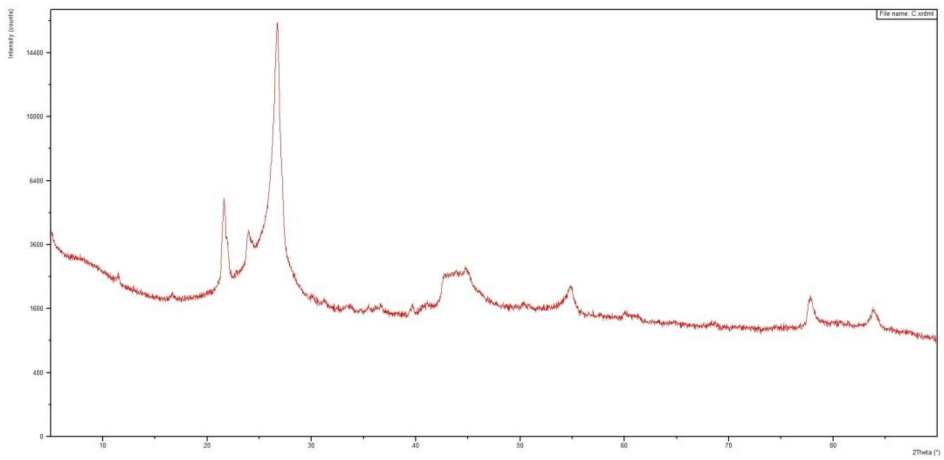

Figure 1 XRD pattern of graphite nanoparticles.

Figure 2 Graphite nanocomposite.

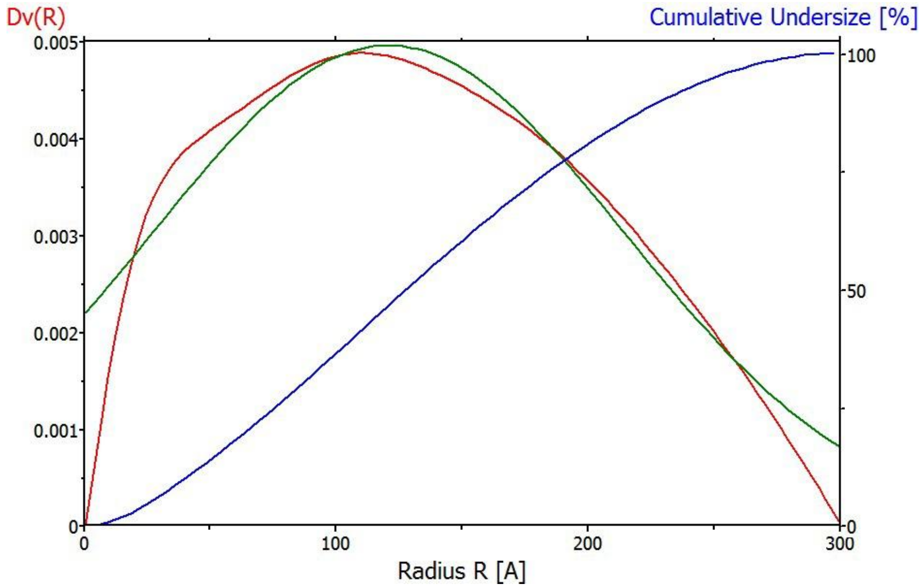

Figure 3 Particle size distribution of graphite nanoparticles.

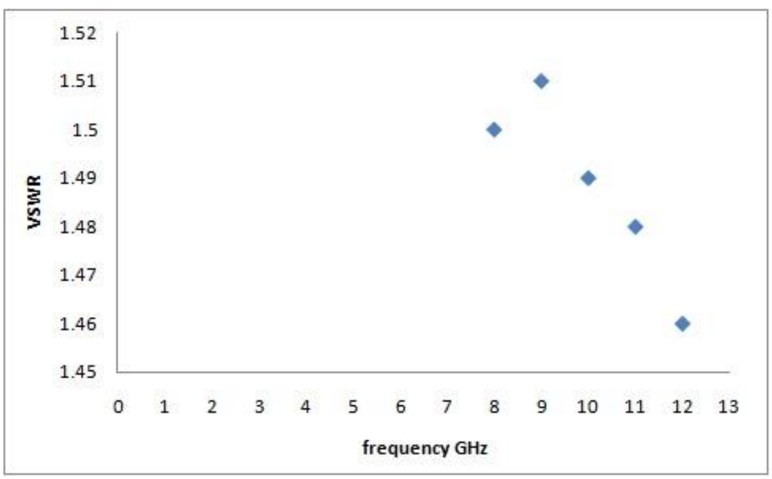

Figure 4 Graph plotted between VSWR and Frequency.

Reflection coefficient vs Frequency:

The values of reflection coefficients and frequency are measured using the microwave bench setup (Klystron Test bench NV9000) for different samples in figure 5 . The graph drawn between reflection coefficient vs frequency shows that reflection coefficient depends on particle size of the material. The nanosheets absorbed nearly 80% of microwave radiation energy for frequencies ranging from 8GHz to 12GHz.

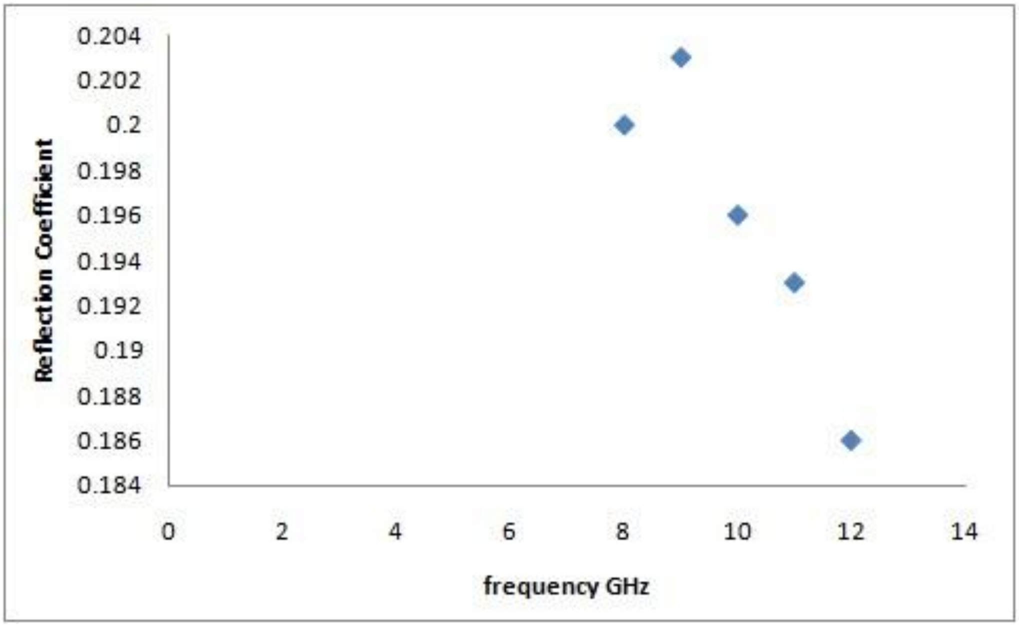

Figure 5 Graph plotted between Reflection coefficient and Frequency.

Return Loss (RL) vs Frequency:

The values of reflection coefficient are measured using the microwave bench (Klystron Test bench NV9000) and return loss (RL) is calculated for graphite nanocomposite as shown in table 1 and figure 6. The graph drawn between return Loss (RL) vs frequency shows that return loss (RL) depends on particle size, crystalline structure and morphology of the material.

The obtained results showed high levels of absorption of electromagnetic energy by structures based on nanoscale graphite nanocomposite prospects of using these structures in the design of real RAM.

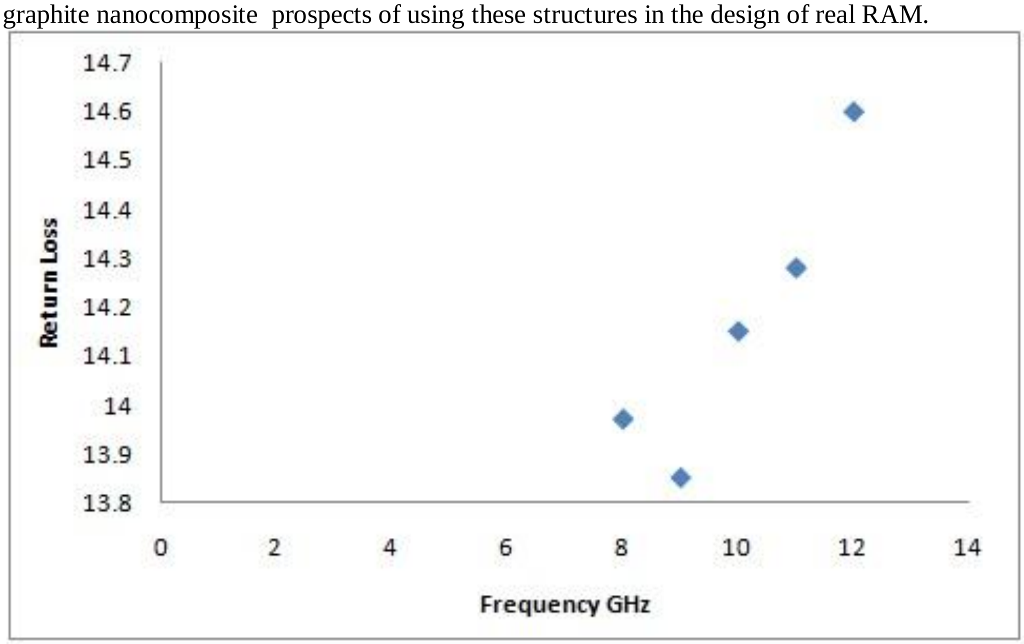

Figure 6 Graph plotted between Return loss and Frequency.

<u>Table 1: Microwave absorption by graphite nanocomposites</u>

Sno	Frequency (GHz)	Power Mode (dB)	VSWR	Reflection coefficient (Γ)	Reflected power (%)	Reflected power (dB)	Absorbed Reflected power (dB)	Return Loss RL
1	8	60	1.50	0.20	33.0	-19.80	40.20	-13.97
2	9	60	1.51	0.203	33.1	-19.86	40.14	-13.85
3	10	60	1.49	0.196	32.8	-19.68	40.32	-14.15
4	11	60	1.48	0.193	32.7	19.62	40.38	-14.28
5	12	60	1.46	0.186	32.5	19.50	40.50	-14.60

Discussion:

Nanostructured RAMs possess enhanced absorbing property due to the nanometer size. The morphology and size of the nanostructured RAMs play very important roles in the microwave return loss (RL) of the nanoparticles and, as the degree or extent of the crystallinity increases, the systematic increment in RL appears. The magnetic-dielectric absorbers of nanocomposite RAMs with suitable dielectric and magnetic properties possess high efficiency because of the complex permittivity and permeability that differ from zero. Nanocomposite of inorganic materials RAMs combines better matched characteristic impedance and improved reflection loss of both materials. For nanostructured graphite nanocomposite RAMs, the position of reflectivity peak moves to a lower frequency and the loss factors of composites increases with decrease in particle size of the material . More efficient shielding properties had been observed for graphite nanosheets as compared to larger-sized aggregates of graphite at the same parameters.

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