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Charge transport mechanism of thermally reduced graphene oxide and their fabrication for high performance shield against electromagnetic pollution

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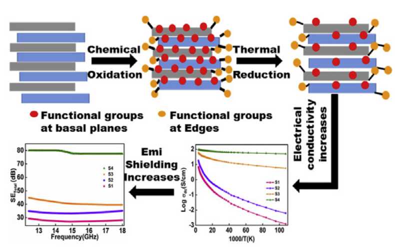
HIGHLIGHTS

- Graphene oxide has been synthesized by Improved Hummer's Method.
- Graphene oxide was reduced at different temperatures.
- The graphene sheets get segregated and dc conductivity increases with reduction.
- The maximum EMI shielding efficiency of 80.81 dB is obtained in highly reduced sample.
- Variable range hopping model is used to explain charge conduction in the samples.

GRAPHICAL ABSTRACT



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ABSTRACT

Shielding devices from thermally reduced graphene oxide have been fabricated for superior electromagnetic interference (EMI) shielding effectiveness. The prepared pristine samples of graphene oxide were reduced at different temperatures. The samples of the thermally reduced graphene oxide were tested in the frequency range of 12.4–18 GHz (Ku band) and the maximum value of EMI shielding efficiency was found to be 80.81 dB for the sample reduced at 1073 K. The charge transport mechanism of thermally reduced graphene oxide samples was also investigated in the temperature range of 10–300 K. The increase in electromagnetic shielding efficiency of thermally reduced graphene oxide samples is attributed to increase in the conductivity and the number of graphitic domains in it. The increase in number of graphitic domains is quantitatively explained on the basis of Tuinstra and Koenig relation. The results show great potential of thermally reduced graphene oxide as a new type of microwave absorbing material.

1. Introduction

Electromagnetic interference (EMI) has emerged as a new kind of pollution. These harmful EM radiations may have harmful effects on the living environment of human beings and can be responsible

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for the degradation in the performance of electronic systems over a long period of time [1–3]. Therefore protection of electronics associated with strategic systems such as aircrafts, communication systems and nuclear reactors is an inevitable requirement. The interaction of the EM radiation with the electronic instruments as well as human environment can be restricted by means of the process of electromagnetic interference (EMI) shielding. A shield can act in two ways against EM radiation, either by total reflection or complete absorption of radiation. The attenuation of EM radiation is exponential when it incidents on the conducting shield. The depth at which the EM field decreases to 1/e of its initial value is called skin depth. An intensive research is going on in the field of high performance and light weight EMI shielding materials [1–4]. The conventional metal (steal, copper and aluminium) based materials have shown very high EMI shielding efficiency of 40–100 dB but they have higher gravimetric mass as compared to light weight carbon materials. Therefore, nowadays, these lightweight materials having high EMI shielding efficiency have gained a lot of attention from various research groups [1–4]. Many organic, inorganic materials and the composites have been widely explored for this purpose. They include carbon nanotubes [5], epoxy/multi-walled composites [6], graphite [7], conducting polymers [8], reduced graphene oxide [2,9,10], zirconium oxide with citric acid [11], tertiary silver/silica/kaolinite nanocomposite [12], graphene wrapped zinc oxide hollow spheres [9] and reduced graphene oxide modified by maghemite colloidal nanoparticle clusters [10]. Reduced graphene oxide is the intermediate step between graphene oxide and graphene. Graphene oxide is a graphene sheet modified with oxygen functional groups such as epoxy, hydroxyl, carboxylic and carbonyl [13–15]. Functional groups decorating the basal plane and the edges of the graphene sheets change the sp^2 hybridization of some carbon atoms to sp^3 hybridization [13–15]. In graphene oxide, majority of carbon atoms bonded to oxygen atoms in sp^3 hybridization, which disrupts the extended sp^2 conjugated network of original graphene sheet. The significant content of sp^3 hybridization is responsible for insulating nature of graphene oxide [16–19]. The removal of oxygen can transform the material into a reduced graphene like semiconductor and ultimately to a graphene like semimetal [20]. Along with graphene, reduced graphene oxide has also gained tremendous attention due to its superior mechanical, electrical, optical, chemical and thermal properties [4,13,14]. Due to these superior properties, it is a promising candidate for many potential applications such as supercapacitor [21], non-volatile memory devices [22], electrochemical and electrochromic devices [23], gas sensors [24] and solar cell devices [25]. Along with these applications, the excellent electrical properties and high surface area [4,13,14] can make reduced graphene oxide a potential material for the electromagnetic shield to absorb incident EM waves. Research suggests that chemically graphitized reduced graphene oxide/silicon dioxide composites exhibit EMI shielding efficiency of 38 dB at 8.5 GHz [2].The EMI shielding effectiveness of 37.58 dB in the frequency range of 12.4–18 GHz is observed in the composite of iron oxide infiltrated reduced graphene oxide with multiwalled carbon nanotubes forest sandwich network [3]. Barium ferrite decorated reduced graphene oxide with an EMI shielding effectiveness of 32 dB in the frequency range of 12.4–18 GHz was also reported [4].The composite of graphene oxide with zinc oxide hollow spheres exhibits a maximum absorption of 45.05 dB at 9.7 GHz [9] and reduced graphene oxide modified by maghemite colloidal nanoparticle clusters composite exhibits the minimum reflection coefficient of −59.65 dB at 10.09 GHz [10]. Unlike reduced graphene oxide, graphene has higher specific EMI shielding effectiveness of 500 dB cm^3 g^{-1} in the frequency range of 30 MHz–1.5 GHz [1], when incorporated in a PDMS matrix. Graphene papers grown by chemical vapour deposition technique have shown excellent EMI shielding effectiveness of 100 dB in the frequency range of 8 GHz–12 GHz [26]. Many reports are available on EMI shielding effectiveness of graphene and reduced graphene oxide. However, there is dearth of data in literature which deals with the high performance microwave absorbing material based on graphene, having good mechanical strength. The graphene deposited by chemically vapour deposition technique is of high quality but has poor mechanical strength. It also requires supporting substrate and expensive catalyst template which may be barrier for industrial application [1].

In the present investigations, we report a systematic study of the thermal reduction of graphene oxide to optimize its conductivity for the improvement in EMI shielding applications. The obtained results focus on the chemical structure of the graphene oxide reduced at different temperatures. For the first time, we have explained dc conduction mechanism of thermally reduced graphene oxide samples on the basis of variable range hopping (VRH) model. We have calculated Mott's parameters of thermally reduced samples in the temperature range of 10–300 K. The room temperature dc conductivity of the samples increases with increase in the reduction temperature. It is observed that the most conductive sample has an EMI shielding effectiveness value of 80.81 dB.The results show great potential of thermally reduced graphene oxide as a new type of microwave absorbing material with excellent EMI shielding effectiveness.

2. Experimental

Graphene oxide was synthesized by improved Hummer's method [27,28]. This involves a strong oxidation of graphite flakes in the presence of acid media. The exothermic reaction involves due to consecutive addition of potassium permanganate (18 g) in graphite flakes (3.0 g, Sigma Aldrich), kept in a round bottom flask at ice cold low temperature bath for avoiding excess heating. A mixture of conc. H_2SO_4/H_3PO_4 (360:40 ml) was poured in this solution for the initialization of oxidation process. The solution was stirred for 12 h at 323 K and then cooled at room temperature and poured onto ice (~400 ml). The removal of excess of potassium permanganate was carried out in the presence of 30% H_2O_2 (3 ml). Finally, the solution was washed to remove the supernatant from the oxidised graphite flakes. Washing involves several steps. It includes washing with water, hydrochloric acid, ethanol and ether sequentially. The solid obtained after washing is vacuum-dried for 48 h at 323 K to obtain graphene oxide. Reduction of graphene oxide consists of conventional method of thermal reduction of graphene oxide in the inert gas atmosphere [18].The graphene oxide powder was thermally treated in the environment of flowing Argon (5% of H_2).The pristine sample was heated at temperature of 423 K in Argon (5% of H_2) environment for one hour to obtain sample S1.Similarly the samples S2, S3 and S4 were prepared by heating pristine sample at 573,873 and 1073 K, respectively in the Argon (5% of H_2) environment. The rate and time of heating remain same as that for the sample S1.

The prepared samples were characterized by Renishaw InVia Reflex micro Raman spectrometer with Air cooled argon laser of wavelength ~514.5 nm for the Raman investigation. The molecular structures of prepared samples have been characterized by FTIR spectrum RX I spectrometer by Perkin Elmer. Thermal stability of the samples was analyzed by Pyris Diamond Thermogravimetric Analyzer of Perkin Elmer. Morphologies of the samples were studied by using Transmission Electron Microscope (TEM), Technai G^2 T30, U-Twin by FEI Netherlands and Field Emission Scanning Electron Microscope (FESEM, Tescan, MIRA3), respectively. The dc conductivity of all the reduced samples was measured in the temperature range of 10–300 K with the help of Keithley 6221 DC