Synthesis and Magnetic Properties of FeCo/Edge-Oxidized Graphene Nanocomposites

Jinu Kim · Ki Hyeon Kim∗
Department of Physics, Yeungnam University, Gyeongsan 38541, Korea
Baekil Nam
School of General Education, Yeungnam University, Gyeongsan 38541, Korea
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FeCo/graphene composites were prepared with increasing graphene weight percent. The graphene-oxide sheets employed water-dispersible edge-oxidized graphene with a lateral size of about 2 - 3 μm and an average thickness of below 5 nm. The FeCo/graphene composites were synthesized by using the coprecipitation method. With increasing graphene concentration in the FeCo/graphene composites, the synthesized FeCo nanoparticles were attached on the edge and the plane of the graphene. The saturation magnetizations and coercivities of the FeCo/graphene composites were 152 emu/g, 85 emu/g, 37 emu/g, 13.5 emu/g and 881 Oe, 766 Oe, 567 Oe, 115 Oe for 0 wt.%, 36 wt.%, 53 wt.%, and 69 wt.% of graphene, respectively. The real parts of the permeabilities of the FeCo/graphene composites were about 1.21 (0 wt.%), 1.10 (36 wt.%), 1.06 (53 wt.%) and 1.00 (69 wt.%) at 1 GHz, after which the permeability abruptly decreased with increasing frequency up to 18 GHz.

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I. INTRODUCTION

Two-dimensional graphene oxide (GO) sheets have attracted as one of the most promising materials for industrial applications, which have the physical and chemical characteristics with the theoretical specific surface area, light weight, high thermal conductivity and good electrical conductivity [1,2]. And it has potential for various application such as electronic device, gas sensors, energy storage, wastewater purification and electromagnetic (EM) shield and absorption [1–11]. In EM shield and absorption, complex permeability and permittivity are fundamental physical properties for determining the EM wave reflection or attenuation and also play a key role in electromagnetic materials to verify the magnetic loss and dielectric loss, respectively [9]. Recently, polymeric nanocomposites with magnetic particles and graphene have been reported for EM shield and absorption application [9–11]. The presence of functional groups of GO sheets enables GO to form stronger bonds with various filler materials and aid the interfacial load transfer between GO and filler materials [12]. In general, reflection and absorption are the dominating factors for EM shielding effectiveness [13]. It results from the combination of the permittivity and permeability values in composite. The permittivity and permeability are deeply related with electrical conductivity and magnetic filler of composite, respectively [14]. The hybrid graphene-magnetic composites can be synthesized by using the magnetic particles and GO. The magnetic and dielectric loss can be controlled by the combination of quantity of graphene and magnetic fillers. We employed the FeCo...
nanoparticles as magnetic fillers. It is one of good candidate material with high saturation magnetization and permeability [15–17]. Therefore, we synthesized the FeCo/graphene nanocomposites with the change of graphene weight percentage to the magnetic fillers and investigated the magnetic properties and complex permeability and permittivity behaviors in GHz frequency region.

II. EXPERIMENTS

FeCo/graphene composites were synthesized by co-precipitation method as shown in Fig. 1. The water dispersible edge-oxidized graphene (EOG, MExplorer Co. Ltd) was employed with lateral size of about 2 - 3 μm and average thickness of below 5 nm. The graphene was dispersed by sonication in deionized water during 1h. The metal salts iron chloride hexahydrate (FeCl$_3$·6H$_2$O) and cobalt chloride hexahydrate (CoCl$_2$·6H$_2$O) were dissolved into deionized water and then mixed with graphene solution at 70 °C under nitrogen gas flowing. Fe to Co molar ratio was fixed 7 to 3 and the molar ratio of graphene to metallic salts was 0, 0.5, 1 and 2. The dissolved sodium borohydride (NaBH$_4$, 135 mmol) in deionized water as a reducing agent was dropped into the metal salts with graphene solution using a dropping funnel over 5 min and then reacted during 30 min. The resulting pH values were approximately 8.9. The FeCo/EOG particles were centrifuged and then dried in vacuum oven 50 °C for 24 hrs.

The weight fractions of graphene were 0 wt.%, 36 wt.%, 53 wt.% and 69 wt.% in the synthesized FeCo/graphene composites, respectively.

The structural phase was examined by using X-ray diffraction (XRD, X’Pert PRO, PANalytical) with Cu Kα radiation (1.54 Å). It confirmed the morphology of the FeCo/graphene composites by using Transmission electron microscopy (TEM, HITACHI, H-7600). The magnetic properties were measured by using a vibrating sample magnetometer (VSM, Lakeshore 7410) at room temperature. The complex permeability and permittivity of FeCo/graphene composites were measured by vector network analyzer (VNA, HP8510) with 7 mm coaxial waveguide up to 18 GHz.
III. RESULTS AND DISCUSSION

The crystalline structures of FeCo and FeCo/graphene nanocomposites were shown in Fig. 2. The X-ray diffraction peaks of FeCo nanoparticles exhibited the amorphous phase at 44.7° (JCPDS card no. 48-1816 and 48-1817). The peaks of FeCo nanoparticles in FeCo/EOG nanocomposites also showed amorphous phase, which peaks were broaden with increasing EOG wt.%. It means that the FeCo nanoparticles should be restricted with increasing EOG wt.%. FeCo nanoparticles were mainly combined with the edge side of graphene by TEM images of FeCo/graphene nanocomposites as shown in Fig. 3. FeCo nanoparticles exhibited the aggregated chain-like structure as shown in Fig. 3(a). As the graphene ratio increases in FeCo/EOG composites, FeCo nanoparticles over 53 wt.% of EOG showed the clustering behaviors from the chain-like structure as shown in Fig. 3(c) and (d). The saturation magnetizations ($M_s$) of FeCo nanoparticles exhibited the 152 emu/g as shown in Fig. 4.

This value is much less than that of the bulk value (245 emu/g), which would be caused by amorphous phase. These magnetization values can be increased due to the heat treatment. The saturation magnetization of FeCo in FeCo/EOG composite were decreased from 152 emu/g to 13.5 emu/g with increasing EOG wt.% from 0 wt.% to 69 wt.%. The remanent magnetization ($M_r$) and coercivity ($H_c$) of FeCo in FeCo/EOG nanocomposites also were decreased from 56.2 emu/g to 1.4 emu/g, and from 881 Oe to 115 Oe, respectively as shown in Fig. 5. The coercivity values of FeCo were decreased with the increment of EOG contents, it would be caused that the agglomerated FeCo particles were reduced due to the increasing EOG content in composites. Also, the size and shape of FeCo nanoparticles can affect to the frequency dependence of permeability and permittivity. The complex permeability and permittivity of FeCo/graphene
composite were measured by 7 mm coaxial line from 1 GHz to 18 GHz. To measure the frequency dependence of complex permeability and permittivity, FeCo/EOG composite were mixed with the paraffin of 50 wt.% and then pelletized the toroidal shape with the thickness of about 1.5 mm. The real part of permeability ($\mu'$) of FeCo/graphene composites exhibited about 1.21, 1.10, 1.06 and 1.00 at 1 GHz with increasing EOG wt.% (0 wt.%, 36 wt.%, 53 wt.%, and 69 wt.%) as shown in Fig. 6(a). Although the real part of permeability decreased with the increment of graphene content below about 2 GHz, this behavior was not followed over 2 GHz. The imaginary part of permeability ($\mu''$) values of FeCo/EOG nanocomposites were fluctuated from 0.03 to 0.65 overall the frequency as shown in Fig. 6(c). The real part of permittivity ($\varepsilon'$) of FeCo/EOG composites exhibited about 8.3, 111.9, 89.0 and 67.9 at 1 GHz with the increment of EOG wt.% as shown in Fig. 6(b). The real part of permittivity values were decreased with the increment of EOG wt.%. The imaginary part of permittivity ($\varepsilon''$) of FeCo/EOG composites showed the wide range from 6.8 to 140 at 1 GHz, which are much larger...
values than that of FeCo composite (0.16 at 1 GHz) as shown in Fig. 6(d). Especially, the imaginary part of permittivity of the 69 wt.% EOG was abruptly decrease with the increment of frequency, and the values were less than that of 36, 53 wt.% of EOG over around 8 GHz. The magnetic loss and dielectric loss can be expressed as \( \tan \delta_m = \frac{\mu''}{\mu'} \) and \( \tan \delta_e = \frac{\varepsilon''}{\varepsilon'} \), respectively. The magnetic loss and dielectric loss of FeCo/EOG composites relatively increased in comparison with that of FeCo without graphene overall the frequency region as shown in Fig. 7(a) and (b). The magnetic loss of FeCo/EOG composites increased with the increase of frequency. The dielectric loss of the FeCo/EOG composite of 69 wt.% exhibited maximum values (about 4.39 at 2.8 GHz).

IV. CONCLUSIONS

The FeCo nanoparticles and the FeCo/EOG composites synthesized by coprecipitation method with increasing EOG wt.%. The FeCo nanoparticles without EOG and FeCo/EOG nanocomposites were exhibited amorphous phase. The saturation magnetizations decreased from 150 emu/g to 13.5 emu/g with the increment of EOG wt.% up to 69 wt.%. Although the real part of permeability values were not so changed with the range of from about 1 to 1.2 at 1 GHz, they were not proportional to the EOG wt.% with the increase of frequency up to 18 GHz. It would be caused by that EOG and magnetic particles were not evenly dispersed in composite. The magnetic loss and dielectric loss relatively increased with the increment of EOG wt.% in FeCo/EOG nanocomposites. The mechanism of the relationship between frequency dependency of the dielectric/magnetic behaviors and the magnetic properties of the FeCo filler is very complicated and not clear with the increment of EOG contents in magnetic-EOG hybrid composite. Therefore, we will further study and analyze the electromagnetic behaviors of magnetic-EOG hybrid composites.

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REFERENCES