Theoretical exploration of optical response of Fe₃O₄-reduced graphene oxide nanoparticle system within dynamical mean-field theory

M A Majidi¹, R Kusumaatmadja¹, A D Fauzi¹, W Y Phan¹, A Taufik¹, R Saleh¹ and A. Rusydi²,³

¹Department of Physics, Faculty of Mathematics and Natural Sciences Universitas Indonesia, Kampus UI Depok, Depok 16424, Indonesia
²NUSNNI-NanoCore, Department of Physics, Faculty of Science, National University of Singapore, Singapore 117576, Singapore
³Singapore Synchrotron Light Source, National University of Singapore, Singapore 117603, Singapore

Corresponding author’s email: aziz.majidi@sci.ui.ac.id

Abstract. We theoretically investigate the optical conductivity and its related optical response of Fe₃O₄-reduced graphene oxide (rGO) nanoparticle system. Experimental data of magnetization of the Fe₃O₄-rGO nanoparticle system have shown that the saturation magnetization can be enhanced by controlling the rGO content with the maximum enhancement reached at the optimal rGO content of about 5 weight percentage. We hypothesize that the magnetization enhancement is due to spin-flipping of Fe ions at tetrahedral sites induced by oxygen vacancies at the Fe₃O₄ nanoparticle boundaries. These oxygen vacancies are formed due to adsorption of oxygen atoms by rGO flakes around the Fe₃O₄ nanoparticle. In this study, we aim to explore the implications of this effect to the optical response of the system as a function of the rGO content. Our model incorporates Hubbard-repulsive interactions between electrons occupying the e_g orbitals of Fe³⁺ and Heisenberg-like interactions between electron spins and spins of Fe³⁺ ions. We treat the relevant interactions within mean-field and dynamical mean-field approximations. Our results are to be compared with the existing experimental reflectance data of Fe₃O₄ nanoparticle system.

1. Introduction
Fe₃O₄, also known as magnetite, has long been investigated most notably for its unique magnetic characteristics and the related potential applications [1]. One of the research directions being pursued by many researchers is to enhance the saturation magnetization. Magnetization of bulk Fe₃O₄ is known to be limited due to its ferrimagnetic structure [2, 3]. Namely, the face-centered-cubic inverse spinel crystal structure of Fe₃O₄ makes two Fe ions at the octahedrally coordinated sites in each formula unit favor to align in the same direction while the remaining Fe ion at the tetrahedrally coordinated site favors to align oppositely to the other two. Recently, a magnetization measurement on a mixture of Fe₃O₄ nanoparticles and reduced graphene oxide (rGO) flakes has shown that the mixture can have saturation magnetization higher than that without the presence of rGO, and it reaches a maximum magnetization enhancement at 5 wt% rGO content [4]. In another theoretical study we propose a hypothesis that the rGO flakes...
located nearby each Fe₃O₄ nanoparticle cluster adsorb some oxygen atoms from the surface of the Fe₃O₄ nanoparticle cluster during the synthesis of the sample, causing formation of oxygen vacancies on the surface of the cluster. According to a previous experimental study [5], which is supported by a theoretical study following it [6], oxygen vacancies in nano-Fe₃O₄ material can induce spin flipflops of the Fe ions located at the tetrahedrally coordinated sites around the oxygen vacancies, which in turn enhances the magnetization of the nano-Fe₃O₄ material. Meanwhile, graphene is a thin layer of carbon in the form of two-dimensional honeycomb lattice. Researchers found that setting adatoms on graphene has been a promising breakthrough because it could tailor the electronic properties of graphene, such as transport, optical and magnetic properties [7]. The hypothesis that rGO tends to adsorb oxygens is motivated by an experimental study on graphene exposed with oxygen plasma [8], and a previous theoretical study on graphene with adatoms [9].

Here, we propose to explore implications of the magnetization enhancement of the Fe₃O₄-rGO nanoparticle system on the optical response of the system. We model the Fe₃O₄ system without and with oxygen vacancies as proposed in reference [6]. While, for the rGO, we use a model for graphene with adatoms as proposed in reference [9]. In addition, we also formulate how the total optical conductivity evolves a function of rGO content. Our calculation result of the optical response of pure Fe₃O₄ nanoparticle system surprisingly shows a very good agreement with the available experimental data. While, the calculation results for the mixture of Fe₃O₄ and rGO nanoparticles need to be verified with more experimental data.

2. Model and method

We use the model Hamiltonian proposed in reference [6] to describe the systems of Fe₃O₄ without and with oxygen vacancies, and the model of graphene with oxygen adatoms proposed in Ref. [9] to represent an rGO layer in an rGO flake. Here we assume that as soon as the nanoparticles are distributed in the sample at the end of the synthesis process there occurs oxygen adsorption from the surfaces of the Fe₃O₄ nanoparticle cluster by the rGO flakes located nearby the Fe₃O₄ nanoparticle cluster. This leads to formation of oxygen vacancies on the surfaces of the Fe₃O₄ nanoparticle clusters. It is then assumed that every unit cell of Fe₃O₄ on the surface of the Fe₃O₄ nanoparticle cluster carrying an oxygen vacancy undergoes a spin flipping that causes its net magnetic moment in the unit cell to enhance by a factor of 3 compared to that of the unit cell that does not have an oxygen vacancy. The overall system is then assumed to consist of the inner part of Fe₃O₄ nanoparticle clusters that have no oxygen vacancies, the surface part of Fe₃O₄ nanoparticle clusters that have oxygen vacancies, and the rGO flakes represented by graphene layers with oxygen adatoms. Figure 1 illustrates the model of the Fe₃O₄-rGO nanoparticle system we propose.

To explore the optical response of the system, we first calculate the retarded Green functions of each component of the system within the dynamical mean-field theory [10, 11], then using the obtained Green functions we calculate the corresponding optical conductivity. The optical conductivity of Fe₃O₄ nanoparticle clusters without oxygen vacancies, denoted as $\sigma_{1, F}^O(\omega)$, and with oxygen vacancies, denoted as $\sigma_{1, F}^V(\omega)$, are derived using the Kubo formula as implemented in reference [12], based on the model presented in reference [6]. While, the optical conductivity of the rGO, $\sigma_{1, G}(\omega)$, is represented by that of graphene with adatoms as presented in reference [6]. Note that the symbol $\sigma_1$ denotes the real part of the complex optical conductivity.

Based on the consideration explained above, we propose that the total optical conductivity of the Fe₃O₄-rGO nanoparticle system is an additive combination of all the components, that is

$$\sigma_1(x, \omega) = \rho_0(x) \sigma_{1, F}^O(\omega) + (1 - \rho_0(x)) \left[ (1 - \gamma) \sigma_{1, F}^O(\omega) + \gamma \sigma_{1, F}^V(\omega) \right] + 2\beta(x) \sigma_{1, G}(\omega). \quad (1)$$

In equation (1), several variables are introduced as the following: $x$ is the measure of weight percentage of rGO in the nanoparticle system; $\rho_0(x)$ is the probability of finding a space between two neighboring Fe₃O₄ nanoparticle clusters with no rGO flake at all; $\gamma$ is the portion of the unit cells that have oxygen

\[P\]
Figure 1. Cartoon of our model for Fe$_3$O$_4$-rGO nanoparticle system. Blue chunks and black slabs represent Fe$_3$O$_4$ nanoparticle cluster and rGO flake, respectively. Left: Fe$_3$O$_4$ nanoparticle system without rGO flakes. Middle: Fe$_3$O$_4$ nanoparticle system with some rGO flakes. Right: Illustration of oxygen adsorption from Fe$_3$O$_4$ nanoparticle clusters by rGO flakes at the end of the synthesis of the sample.

vacancies in an Fe$_3$O$_4$ nanoparticle cluster; $\beta(x)$, which is a function of $x$, is the ratio of the total number of existing rGO layers to the total number of "rGO slots" in all spaces between two neighboring Fe$_3$O$_4$ nanoparticle clusters in the sample. Statistically, $P_0(x)$ depends on $\beta(x)$ in the following way

$$P_0(x) = (1 - \beta(x))^n,$$

(2)

where $n$ is the maximum number of rGO layers filling the space between two neighboring Fe$_3$O$_4$ nanoparticle clusters above which no empty spaces between two neighboring Fe$_3$O$_4$ nanoparticle clusters can be found. $\beta(x)$ itself depends on $x$ in the following manner

$$\beta(x) = \frac{\alpha x}{2(1-x)},$$

(3)

where $\alpha$ is the ratio between mass of an Fe$_3$O$_4$ nanoparticle cluster and mass of an rGO layer.

As we aim to compare our results with experimental data available in the form of reflectance, we need to convert our formula of optical conductivity to reflectance. This can be done as the following. First, having the real part of the complex optical conductivity, $\sigma_1(\omega)$ for the whole spectrum of photon energy, we can compute the corresponding imaginary part, $\sigma_2(\sigma)$, through the Kramers-Kronig relation

$$\sigma_2(\omega) = \frac{2\omega}{\pi} \int_0^\infty d\omega' \frac{\sigma_1(\omega')}{\omega'^2 - \omega^2}.$$  

(4)

Knowing the complex optical conductivity, $\sigma(\omega) = \sigma_1(\omega) + i\sigma_2(\omega)$, we can calculate the complex dielectric function through the relation

$$\varepsilon(\omega) = \frac{i}{\varepsilon_0 \omega} (\sigma_1(\omega) + i\sigma_2(\omega)).$$

(5)

The complex dielectric function itself is related to the complex refractive index through

$$n(\omega) + i\kappa(\omega) = \sqrt{\varepsilon(\omega)}.$$  

(6)
Figure 2. Calculation results of optical conductivity at a room temperature. Top-left: Fe$_3$O$_4$ without oxygen vacancies, top-right: Fe$_3$O$_4$ with oxygen vacancies; bottom-left: rGO with various adatom concentrations and positions chemical potential; bottom-right: Fe$_3$O$_4$-rGO system at various wt% of rGO.

Finally, the reflectance, $R(\omega)$, is defined as

$$R(\omega) = |r(\omega)|^2 = \left| \frac{n(\omega) + i\kappa(\omega) - 1}{n(\omega) + i\kappa(\omega) + 1} \right|^2 = \frac{\sqrt{\varepsilon(\omega) - 1}}{\sqrt{\varepsilon(\omega) + 1}}^2. \quad (7)$$

3. Results
Comparing between the top-left and the top-right of figure 2, especially in the low energy region, our calculation results of optical conductivity at a room temperature show that Fe$_3$O$_4$ without oxygen vacancies has a Drude peak indicating the metallic (more precisely half-metallic) character, whereas Fe$_3$O$_4$ with oxygen vacancies is an insulator or semiconductor. Meanwhile, the bottom-left figure shows the optical conductivity profile of graphene with adatoms at various values of adatom concentration ($x$) and chemical potential ($\mu$). The bottom-right figure shows our prediction of optical conductivity profile of the Fe$_3$O$_4$-rGO nanoparticle system for various wt% values of rGO.

The left panel of figure 2 shows the comparison between the calculated reflectance of Fe$_3$O$_4$ system without oxygen vacancies and the experimental data of Fe$_3$O$_4$ nanoparticle system without rGO [4].
Figure 3. Left: Calculated reflectance of Fe$_3$O$_4$ without oxygen vacancies and the corresponding experimental data Fe$_3$O$_4$ nanoparticle system for comparison. Right: Calculated reflectance of Fe$_3$O$_4$-rGO nanoparticle system at various wt% values of rGO.

There we can see a very good similarity of the trend of the two curves. In particular, both curves agree very well even quantitatively in the region of 2.5-6 eV. We argue that this is a strong indication of the legitimacy and adequacy of our model. One little discrepancy appears in the width of the zero-frequency peak, for which our calculation result gives a too small width compared to that of the experimental data. However, this is not a very crucial discrepancy as we believe a further fine-tuning of our model parameters could remedy this problem. Based on the consideration just discussed, on the right panel of figure 2 we present our prediction of the reflectance of the Fe$_3$O$_4$-rGO nanoparticle system for various wt% values of rGO, that we hope to be able to compare with experimental data in the near future.

4. Conclusions

In conclusion, we have developed a model to predict the optical response of the Fe$_3$O$_4$-rGO nanoparticle system for various wt% of rGO, as an implication of the phenomenon of magnetization enhancement occurring in the system upon the addition of rGO flakes into the Fe$_3$O$_4$ nanoparticle system. The very good qualitative agreement of the calculated reflectance curve of the Fe$_3$O$_4$ system without oxygen vacancies may strongly indicate that the model of Fe$_3$O$_4$ system is adequate as a starting point, and hence the calculation results for the optical conductivity or the reflectance of the Fe$_3$O$_4$-rGO nanoparticle system are worthy of experimental verification.

Acknowledgement

We gratefully acknowledge the full funding support provided by Universitas Indonesia, Indonesia, for the completion of this project through PITTA Research Grant No. 2022/UN2.R12/HKP.05.00/2016.

References

[1] Gutfleisch O, Willard M A, Brück E, Chen C H, Sankar S G and Liu J P 2010 Adv. Mater. 23 821–42
[2] Néel L 1948 Ann. Phys. 3 137
[3] Smit J and Wijn H P J 1959 Ferrites (Eindhoven: Philips’ Technical Library)
[4] Taufik A and Saleh R 2016 AIP Conf. Proc. 1725 020089
[5] Herng T S et al. 2015 Nano Res. 8(9) 2935–45
[6] Fauzi A D, Majidi M A and Rusydi A 2017 J. Phys.: Condens. Matter 29 135802
[7] Neto A H, Kotov V N, Nilsson J, Pereira V M, Peres N M R and Uchoa B 2009 Sol. State Comm. 149 1004
[8] Santoso I, Singh R S, Gogoi P K, Asmara T C, Wei D, Chen W, Wee A, Pereira V M and Rusydi A 2014 Phys. Rev. B 89 075213

[9] Majidi M A, Siregar S and Rusydi A 2014 Phys. Rev. B 90 195442

[10] Georges A, Kotliar G, Krauth W and Rozenberg M 1996 Rev. Mod. Phys 68

[11] N. Furukawa, J. Phys. Soc. Jpn. 63, 3214 (1994); in Proceedings of the International Conference on Physics of Manganites, Michigan State University, 1998, edited by Kaplan T A and Mahanti S D (Kluwer Academic/Plenum, New York, 1998), p. 1.

[12] Majidi M A, Su H, Feng Y P, Rübhausen M and Rusydi A 2011 Phys. Rev. B 84 075136