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Enhanced Terahertz Emission from Quantum Dot by Graphene-coated Nanoparticle

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Enhanced Terahertz emission from quantum dot by graphene coated nanoparticle

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Abstract

The Terahertz (THz) emission from quantum dots in close proximity to graphene coated nanoparticles is studied via phenomenological modeling with particular interest in the possibility of enhancement for such emission via the excitation of the graphene plasmons. It is shown that depending on various factors such as the damping factor and the Fermi level of the graphene, as well as the size and core material of the coated particle, such plasmonic enhanced THz emission is indeed possible. This thus opens up a new pathway to provide intense THz sources for future applications.

Key Words: THz emission, plasmonic enhancement, graphene coated nanoparticles

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1. Introduction

Recent advances in Terahertz (THz) technology have led to significant novel applications in many different areas such as communication, spectroscopy, and imaging [1, 2]. Although various electronic and optical methods for THz generation have been developed in time, highly intense sources at such emission frequencies are constantly in demand for various applications [3]. Among these sources, semiconductor nano structures have been recognized as systems with high potentials and various mechanisms have been studied for the enhancement of the THz emissions from these systems [4]. For example, a recent study has demonstrated plasmonic enhancement using metallic nanoparticles is possible for the THz emission from self-assembled quantum dot (QD) molecules [5].

While the plasmonic frequencies of metal are mostly in the visible or UV range, which leads to the enhancement at THz rather indirect (e.g. via the coupling between the two QD's in the "molecule" [5]), one is tempted to explore alternative plasmonic systems at lower frequencies for such an application. One such possibility is to employ graphene plasmonics [6], which has been intensively studied by many researchers in the literature due to the unique properties in the collective motion of the p electrons in the graphene [7, 8]. Moreover, a recent investigation employing planar single-layer graphene for the enhancement of CdTe/ZnS QD emission has reported only multiphoton emission enhancement, with fluorescence intensity actually *reduced* due to the decrease in QD radiative decay rate in the proximity of the graphene [9]. Nevertheless, there exist other graphene nano-structures which may effect differently on their plasmonic enhancement of QD emissions. In particular, several very recent studies have demonstrated that plasmonic

resonances from THz to NIR can be excited from nanoparticles coated with a monoatomic layer of graphene [10 -12].

It is thus the purpose of the present work to study theoretically the possibility of using these graphene-coated nanoparticles (GCNP) to enhance the THz emission from various single QD's. This is in analogy with previous studies in the literature on the control of various dye emissions using metallic nanoparticles [13]. We will see that via the control of various parameters of this QD-GCNP system, enhanced THz emissions from the QD can indeed be achieved provided that the damping of the p electrons is small enough. For simplicity, the QD will be modeled as a point dipole which is justified for QD sizes being small compared to that of the GCNP which will be in the tens of nanometers [5].

2. Theoretical model

2.1 Electrodynamics for the dipole-GCNP problem

Our problem is as depicted in Fig. 1 which shows a point dipole emitting in the vicinity of a GCNP which contains a monoatomic graphene shell coated on a spherical core of dielectric constant e_C and radius R. In the recent work by Christensen et al [10], the authors have derived the optical response of a graphene-coated nanosphere by accounting for the graphene monolayer shell as one of negligible thickness and with its optical properties characterized by the following isotropic and local (i.e. only frequency dependent) surface conductivity function:

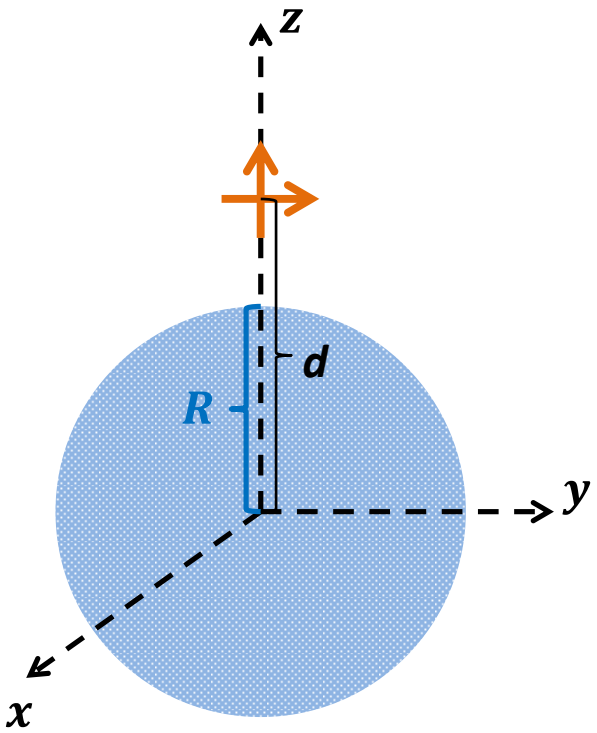

Fig. 1 Configuration of the problem.

$$s(w) = s_{\text{intra}}(w) + s_{\text{inter}}(w) \tag{1}$$

with each of the intraband and interband terms expressed in the following forms:

$$\begin{aligned} \sigma_{\text{intra}} &= \left(\frac{e^2}{\pi\hbar}\right)\left(\frac{2ik_BT}{\hbar\tilde{\omega}}\right)\ell n\left[2\cosh\left(\frac{\varepsilon_F}{2k_BT}\right)\right], \\ \sigma_{\text{inter}} &= \left(\frac{e^2}{\pi\hbar}\right)\left[\left(\frac{\pi}{4}\right)H\left(\frac{1}{2}\hbar\omega\right) + i\hbar\tilde{\omega}\int_0^\infty d\varepsilon \frac{H(\varepsilon) - H(\frac{1}{2}\hbar\omega)}{\hbar^2\tilde{\omega}^2 - 4\varepsilon^2}\right], \end{aligned} \tag{2}$$

where $\tilde{\omega} \equiv \omega + i\gamma_g$ with g_g being the optical loss rate of graphene, $\left(e^2/\pi\hbar\right)$ the quantum conductance, k_BT the thermal energy, e_F the Fermi energy, and $H(e) = \sinh(e/k_BT)/\left[\cosh(e_F/k_BT) + \cosh(e/k_BT)\right]$ is the population difference between energies e (see Ref. [10]). It was further justified that the results in (2)

originally established for planar graphene structures can be extended for spherical geometry as long as the curvature is small satisfying $k_F R \gg 1$ where k_F is the Fermi vector. This latter condition is assured in most of our numerical studies below (e.g. for $e_F = 0.1$ eV and $R = 20$ nm, $k_F R \sim 10$).

Hence, within this model, the full electrodynamics of the dipole-GCNP problem can be solved in a way exactly parallel to that of the Ruppin theory for a dipole-sphere system [14], except that one of the boundary conditions for the continuity of the tangential magnetic field must be replaced by a discontinuity due to the presence of a surface current originated from the conductivity in (1) in the form $\vec{K} = \sigma \vec{E}$ in the presence of an external electromagnetic field. However, this is thus exactly the same situation for a dipole interacting with a sphere carrying a surface charge which can be characterized by a surface conductivity [15]. Such a problem has been solved in our previous work via a combination of Ruppin's theory [14] and the modified Mie theory by Bohren and Hunt for a charged sphere [15]. We provide a brief summary of our previous solution as follows (see [16] for details).

By going through Ruppin's solution with the following modified boundary conditions:

$$\mathbf{n} \times (\mathbf{E}_1 - \mathbf{E}_2) = \mathbf{0}, \tag{3}$$

and

$$\mathbf{n} \times (\mathbf{H}_1 - \mathbf{H}_2) = \mathbf{K}, \tag{4}$$

we have shown [16] that *all* the results obtained in Ruppin's theory for a dipole-neutral sphere system can be applied to the charged sphere case, provided that the Mie

coefficients used in Ruppin's theory are replaced by the following generalized ones as obtained in the work of Bohren and Hunt [15]:

$$a_n = -\frac{\psi_n'(x)\psi_n(mx) - \psi_n(x)\left[m\psi_n'(mx) - i\tau\psi_n(mx)\right]}{\xi'(x)\psi_n(mx) - \xi_n(x)\left[m\psi_n'(mx) - i\tau\psi_n(mx)\right]}, \tag{5}$$

$$b_n = -\frac{\psi_n(x)\psi_n'(mx) - \psi_n'(x)\left[m\psi_n(mx) + i\tau\psi_n'(mx)\right]}{\xi_n(x)\psi_n'(mx) - \xi'(x)\left[m\psi_n(mx) + i\tau\psi_n'(mx)\right]}, \tag{6}$$

where ψ_n, ξ_n are the Riccati-Bessel functions, $x = kR$ is the size parameter of the sphere, $m = \sqrt{e_C}$ is the refraction index of the core of the (nonmagnetic) sphere, and $t = \frac{4p}{c}s(w)$ is the "charge parameter" in terms of a surface conductivity (in Gaussian units) and c is the speed of light. Hence all our previous results for the dipole-charged sphere problem can be applied to the present dipole-GCNP problem simply by using Eqs. (1) and (2) for the "surface conductivity" from the previous theory [10]. We emphasize here that although there have been many previous calculations of optical response of graphene in the literature using the surface conductivity concept, we are not aware of any previous study of the dynamical interaction between a source dipole and a GCNP using such an approach.

2.2 Calculation of emission characteristics

To be self-contained, for the calculation of the characteristics of the emitting dipole near a GCNP, we collect the equations from our previous work for the emission and decay rates of the dipole as follows [16]:

For the emission rate, we have:

$$g_E = \left|\frac{E}{E_0}\right|^2 \left(\frac{g_r}{g_r + g_{nr}}\right), \tag{7}$$

where $\left|E / E_0\right|^2$ is the field enhancement ratio and

$$Y = \frac{\gamma_r}{\gamma_r + \gamma_{nr}} \tag{8}$$

is the quantum yield of the emitting dipole in the presence of the GCNP. Note that $\left|E / E_0\right|^2$ also describes the excitation probability of the dipole in the absence of saturation of emission, and Y indicates the probability of receiving the emitted photons in the far field (radiation efficiency), where γ_r and γ_{nr} are the radiatve and nonradiative decay rates, respectively. From our previous modified Ruppin theory [14, 16], we have:

For a radial oriented dipole:

$$\frac{E}{E_0} = 1 + \sum_{n=1}^{\infty} i^{n+1} b_n (2n+1) P_n^1(0) \frac{h_n(x_d)}{x_d}, \tag{9}$$

$$\gamma^{\perp} = 1 + \frac{3}{2} \mathrm{Re} \sum_{n=1}^{\infty} n(n+1)(2n+1) b_n \left(\frac{h_n(x_d)}{x_d}\right)^2, \tag{10}$$

$$\gamma_r^{\perp} = \frac{3}{2} \sum_{n=1}^{\infty} n(n+1)(2n+1) \frac{\left|j_n(x_d) + b_n h_n(x_d)\right|^2}{x_d^2}, \tag{11}$$

and

$$\hat{g_{nr}} = \hat{g} - \hat{g_r}, \tag{12}$$

where $\gamma^{\perp} = \gamma_r^{\perp} + \gamma_{nr}^{\perp}$ is the total decay rate (all normalized to the free decay value). The various special functions and Mie coefficients are in obvious notations with $x_d = kd$ and d being the distance of the dipole from the sphere center.

For a tangential oscillating dipole:

$$\frac{E}{E_0} = 1 + \sum_{n=1}^{\infty} i^n \frac{2n+1}{n(n+1)} \left\{ a_n P'_n(0) h_n(x_d) + i b_n P_n^1(0) \frac{\left[x_d h_n(x_d) \right]'}{x_d} \right\}, \tag{13}$$

$$\gamma^{\parallel} = 1 + \frac{3}{4} \mathrm{Re} \sum_{n=1}^{\infty} (2n+1) \left[a_n h_n^2(x_d) + b_n \left(\frac{\xi'(x_d)}{x_d} \right)^2 \right], \tag{14}$$

$$\gamma_r^{\parallel} = \frac{3}{4} \sum_{n=1}^{\infty} (2n+1) \left\{ \left| j_n(x_d) + a_n h_n(x_d) \right|^2 + \frac{1}{x_d^2} \left| \psi'_n(x_d) + b_n \xi'_n(x_d) \right|^2 \right\}, \tag{15}$$

and $$g_{nr}^{//} = g^{//} - g_r^{//}. \tag{16}$$

3. Numerical Results

To illustrate how possibly the GCNP can lead to enhanced emission rate for the QD, we have performed some numerical studies by first considering the optimized situation with a "vacuum core" [17]. Since in most practical situations, the orientation of the transition dipole moment of the QD is randomized and has no correlation with the GCNP, we shall only perform calculations averaging over the orientations of the emitting dipoles. Hence, while it is well-known that the radial dipoles will have higher emission yield than that from the tangential dipoles at close QD-GCNP distances [18], here we shall only report with weighted-average results over the dipole orientations with (1/3) weight from radial and (2/3) from tangential contributions in the following.

Figure 2 shows the quantum yield [Eq. (8)] as a function of transition frequency of the QD for a GCNP of 20 nm radius and doped at a Fermi level of 0.4 eV, with a small graphene damping g_g of 1 meV which may not be unrealistic according to some recent literature [19]. The figure shows values only up to the dipole plasmon resonance of the GCNP which is at ~ 0.19 eV (correspond to ~ 50 THz) for three locations of the QD at 1

nm, 5 nm, and 9 nm distance from the GCNP, respectively. As seen from the results, although the graphene plasmon does lead to enhanced quantum yields at resonance, the absolute values are very small (~ 1%) due to high nonradiative rates at such close distances. Moreover, it is interesting to note that the peak value for the yields are rather insensitive to the location of the QD within this range of QD-GCNP distance, although relative large yields occur at father distances off resonance due to the decrease in nonradiative loss to the GCNP.

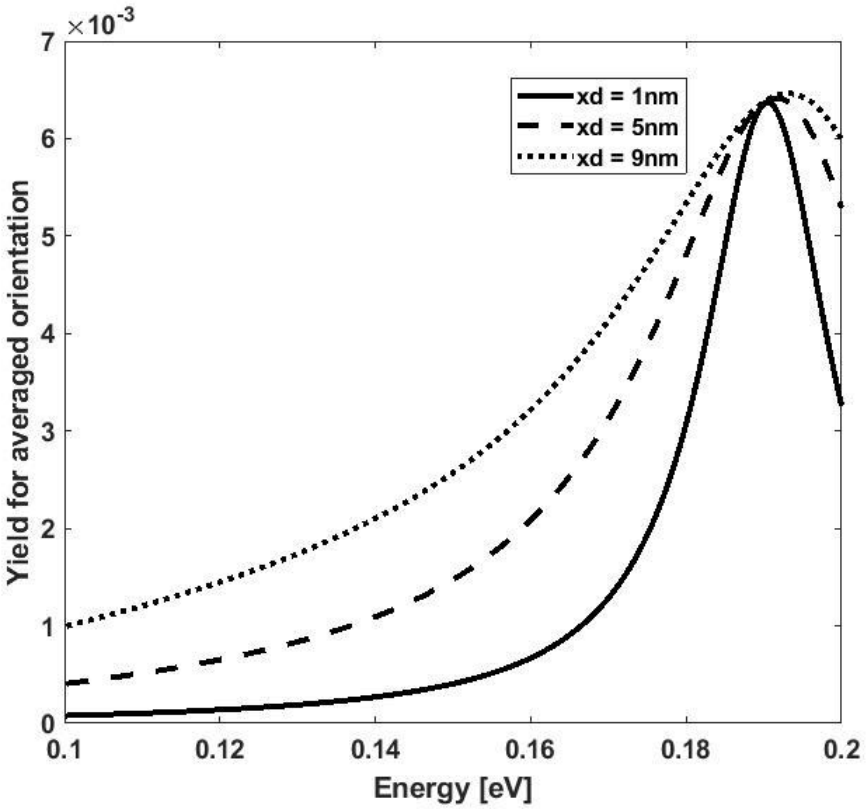

Fig. 2 Quantum yield (Eq. (8)) vs frequency for different dipole distance with a vacuum core.

Nevertheless, despite the low quantum yield at such close distances, we show next the plasmonic enhanced local field intensity [Eqs. (9) and (13)] in Fig. 3, from which we

obtain an enhanced intensity of ~ 10^4 at the dipolar plasmonic resonance of the GCNP. Also noticed is the monotonic decrease in this peak enhancement as the QD is moved away from the GCNP. Thus enhanced emission from the QD is possible within this distance range despite the low quantum yield.

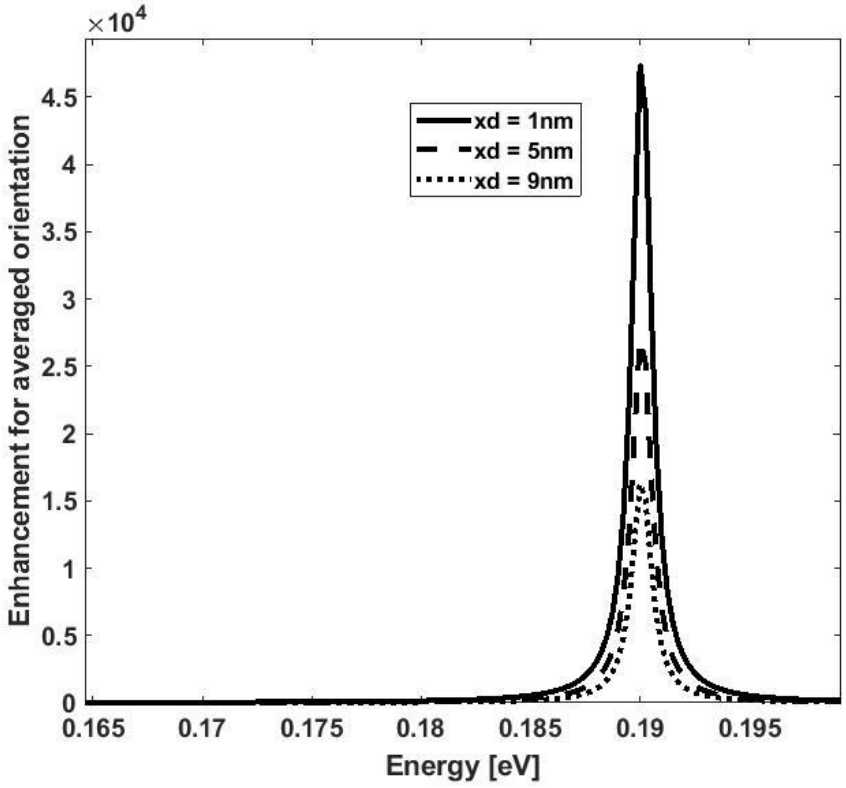

Fig. 3 Field enhancement factor ($\left|E / E_0\right|^2$) vs frequency for different dipole distance and a vacuum core.

To demonstrate this explicitly, we next calculate the overall emission rate [(Eq. (7)] and the results are as shown in Fig. 4, from which it is seen that hundredfold enhancement of the emission is possible at the graphene resonance frequency of ~ 50 THz. Furthermore, a monotonic decrease of the emission peak with QD-GCNP distance is observed which appears to be different from what was observed previously in

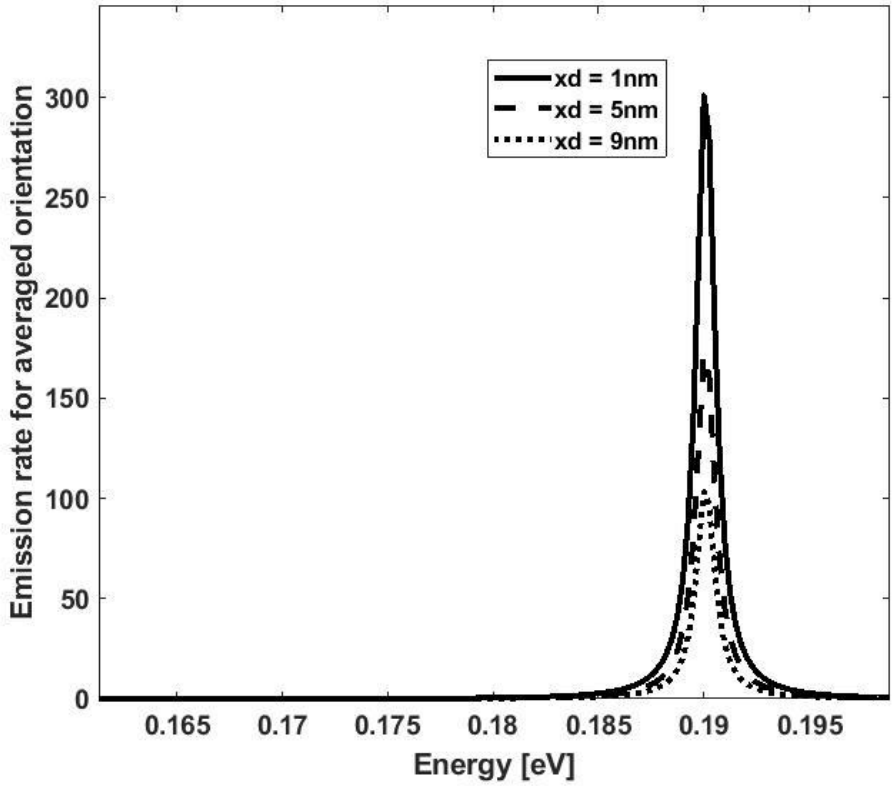

Fig. 4 Emission rate (Eq. (7)) for a vacuum core. Other parameters are the same as in Fig. 2.

experiments with dye molecules near metal nanoparticles in which an optimal distance was observed [20]. We speculate this to be likely due to that the nonradiative rates at very close distance for the GCNP case are not as large as those in the case with metallic nanoparticles.

We thus conclude that GCNP can indeed be used to enhance QD emission at THz frequencies. To demonstrate this with more realistic structures, we show in Fig. 5 results for emission yield with a glass core for the GCNP. In comparison with those in Fig. 4 for a "vacuum core", we see that enhanced emission is still possible with a glass core

although to a less degree of enhancement in such a case. This is expected since part of the energy emitted from the QD is consumed in the polarization of the glass core and a "vacuum core" remains the idealized configuration for optimal enhancements [12].

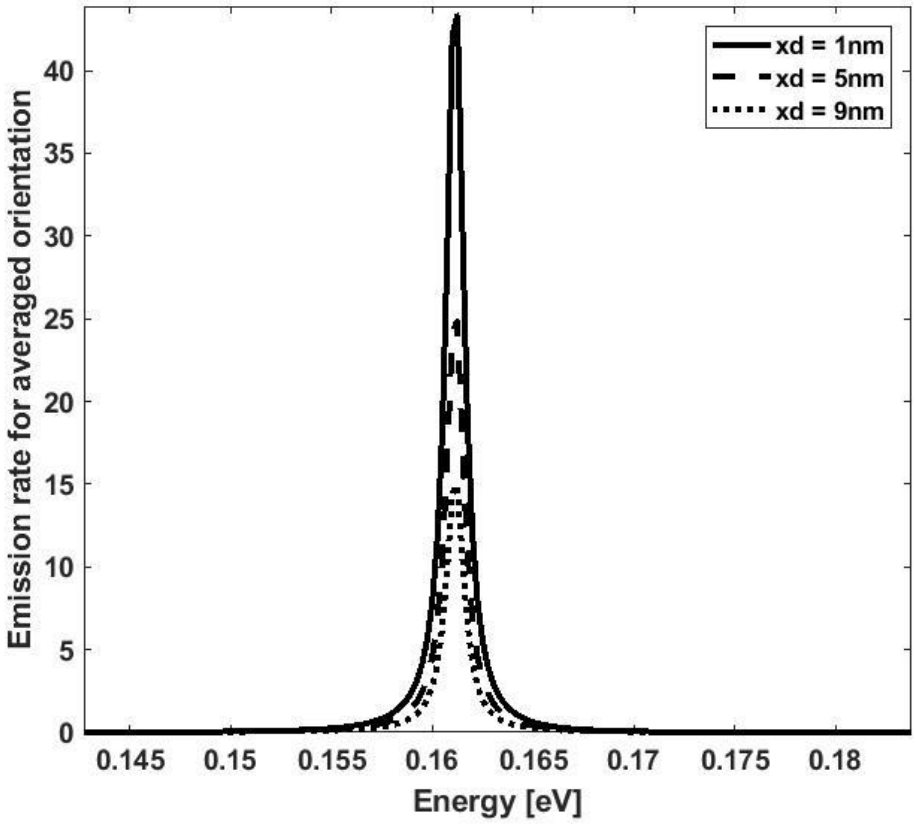

Fig. 5 Emission rate for a GCNP with a glass core. All other parameters are the same as those in Figs. 2-4.

Figure 6 shows the enhanced emission rate for a vacuum core GCNP as a function of the size of the particle, where we have plotted the *peak* rate as a function of the radius at the respective resonance frequency of the sphere with that specific size. Only a close distance of 1 nm is considered here since at farther distances, one only obtains smaller results for the enhanced rates. It is seen that the enhanced rate exhibits an overall

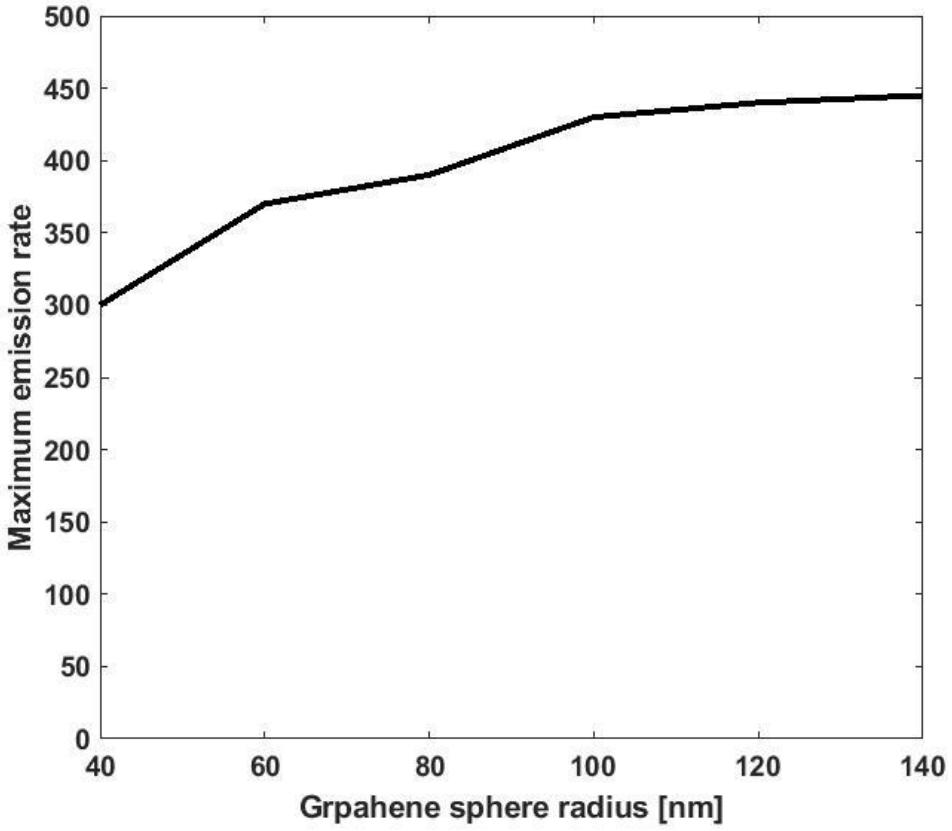

Fig. 6 Maximum emission rate vs graphene sphere radius with averaged dipole orientations and a vacuum core at xd = 1 nm.

Increase with the GCNP size, ultimately shows up with a broad peak around ~ 140 nm in GCNP radius for such a close distance. Such optimal-size induced enhancement for metallic particles has been well-established in the literature [21]. Finally, we study the effects of the doping and damping of the GCNP on the enhanced emission of the QD. Figure 7 shows the emission rate for a vacuum core as a function of the damping constant g_g for three different Fermi energy levels of the graphene. The emitting dipole is fixed at 1 nm from GCNP and its orientation is again averaged. Note that only an appropriate

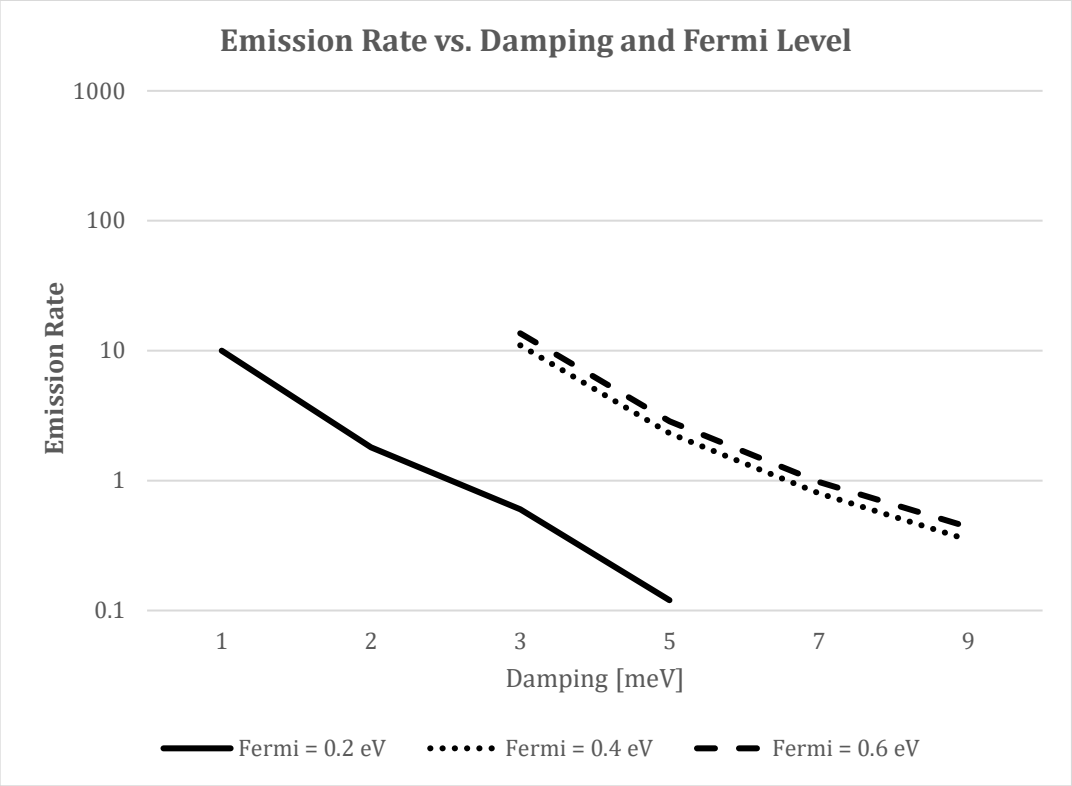

Fig. 7 Enhanced emission rate as a function of the damping and Fermi energy of the graphene.

portion of each curve is shown since our focus here is in the critical damping value beyond which the enhanced rate will go below 1. It is clearly seen that for a fixed doping level (i.e. Fermi energy), there exists a critical damping value beyond which no emission enhancement can be obtained (i.e. with emission rate < 1). In addition, this critical damping will remain roughly insensitive to the doping level when such level increases to around 0.5 eV. Since these critical damping values are in the range of ~ 2 – 7 meV, it further demonstrates this GCNP-enhanced emission can indeed become realistic, for such low damping values can likely be achievable in light of the latest technological advances,

especially at higher doping level of the graphene. Again, for clarity of the figures, we only show results for case with a close QD-GCNP distance of 1 nm. For farther distances, we will expect similar behaviors with smaller enhanced emission rates and slightly greater critical damping values as the emitter is moving away from the GCNP.

4. Discussion and Conclusion

In this paper we have demonstrated the feasibility of using graphene-coated nanoparticles to achieve plasmonic enhancement for THz emission sources like certain quantum dots. We have shown that with the manipulation of various graphene parameters and the core materials, such enhanced THz emission can indeed be obtained. In particular, we have shown that optimum enhancement is possible if the GCNP can have a vacuum core, which may not be too unrealistic since materials like silica aerogel can be fabricated with a refractive index close to unity [22].

Although our simple model has been limited to the consideration of single-QD's interacting with single GCNP's, and in more realistic situations other effects such as those from a substrate or neighboring particles may come into play, the qualitative conclusions from our study should have some general validity. In particular, one can imagine fabricating a system of a colloidal QD solution with a low concentration of GCNP dispersed in it for which our modeling results will be close to reality. In any case, such substrate or inter-particle effects have been investigated over a long period of time in the literature for metallic nanoparticle (MNP) enhancements, and the results have shown that such effects will in general lead to small red-shifts in the resonances together with smaller enhancements, except when the emitter falls between the "particle gaps" where

greater enhancement will result [23, 24]. Furthermore, if nonlocal effects were taken into account, these substrate and inter-particle effects will be further reduced [25]. We expect similar situation will take place when these effects are accounted for in the case when the MNP is replaced by the GCNP. Nevertheless, it will be of interest for future studies to investigate these effects in details as were done for the case with MNP.

Thus in conclusion, the approach explored in our work indeed provides an alternative and more flexible methodology to generate strong THz emissions compared to previous approaches using quantum dot molecules or planar single graphene layers. This should motivate experimentalist to demonstrate such feasibility as proposed in the present work.

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