Giant enhancement of the third harmonic in graphene integrated in a layered structure

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Graphene was shown to have strongly nonlinear electrodynamic properties. In particular, being irradiated by an electromagnetic wave with the frequency \( \omega \), it can efficiently generate higher frequency harmonics. Here we predict that in a specially designed structure “graphene – dielectric – metal” the third-harmonic (3\( \omega \)) intensity can be increased by more than two orders of magnitude as compared to an isolated graphene layer.

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It was theoretically predicted \([1]\) that, due to the “ultra-relativistic”, massless energy dispersion of graphene electrons,

\[
E_{\pm}(k) = \pm \hbar v_F |k|, \tag{1}
\]

it should demonstrate a strongly nonlinear electrodynamic response; here \( v_F \approx 10^6 \) cm/s is the Fermi velocity of graphene and \( k \) is the electron wave-vector. Physically, this is due to the absence of inertia of graphene electrons: According to \([1]\), electrons can move only with the velocity \( v_F \) in any directions, therefore, being placed in the oscillating external electric field they have to “instantaneously” change their velocity from \( +v_F \) to \( -v_F \) in the return points. This leads to the emission of radiation at higher (multiple) frequencies as well as to other nonlinear phenomena. The efficiency of the nonlinear effects in graphene was predicted to be many orders of magnitude larger than in many other nonlinear materials \([1]\).

Experimentally, a strong nonlinearity of the graphene response has been confirmed at microwave \([2]\) and optical \([3]\) frequencies. Further experimental studies of different nonlinear electrodynamic effects in graphene can be found in Refs. \([4\) \(\text{[1]}\)\] A quasi-classical theory of the nonlinear electrodynamic response of graphene, which is valid at relatively low (microwave, terahertz) frequencies \( \hbar \omega \ll 2E_F \), has been developed in Refs. \([1\) \(\text{[1]}\) \(\text{[1]}\)\]; here \( E_F \) is the Fermi energy. This theory takes into account only the intra-band electronic transitions and ignores the inter-band ones. More general, quantum theories, which take into account both contributions, have been recently proposed in Refs. \([\text{19} \text{ [24]}\)\]. It was shown that, apart from a strong resonance at low (\( \hbar \omega \ll 2E_F \)) frequencies, the third-order nonlinear conductivity \( \sigma_{\alpha\beta\gamma\delta}(\omega_1, \omega_2, \omega_3) \) demonstrates a number of resonances at the frequencies corresponding to the one-, two- and three-photon inter-band absorption.

In Refs. \([\text{19} \text{ [24]}\)\] the third-order nonlinear response functions of graphene have been calculated for a single, freely hanging in vacuum (or in air) mono-atomic graphene layer. In reality graphene lies of a dielectric substrate (of thickness \( d \)). In this Letter we study the influence of the dielectric environment on the efficiency of the third harmonic generation and show that, depending on the ratio \( d/\lambda_\omega \), as well as on physical properties of layers supporting graphene, the output third harmonic intensity can be both several orders of magnitude smaller and several orders of magnitude larger than in the isolated graphene layer. A proper choice of the geometrical parameters and physical properties of the dielectric environment is thus vitally important for the successful operation of graphene based nonlinear devices.

As an example, we consider a layered system “graphene – medium 1 – medium 2” where a two-dimensional graphene layer lies at the plane \( z = 0 \) and each of the media is characterized by a thickness \( d_j \) and a complex dielectric permittivity \( \epsilon_{j}(\omega) \), \( j = 1, 2 \). We assume that a linearly polarized (in the \( x \)-direction) electromagnetic wave with the frequency \( \omega \) and the power density \( I_\omega \) is normally incident on the structure from the graphene side, see insets to Figs. \([1\) \(\text{[2]}\) \(\text{[3]}\)\]. The distribution of electromagnetic fields in the system is described by Maxwell equations with the dielectric function \( \epsilon(\omega, z) \), being equal to \( \epsilon_{x}(\omega) \) inside the \( j \)-th layer, and with the term \( j_{\alpha}(t)\delta(z) = \delta_{\alpha xx}j(t)\delta(z) \), describing the current in the two-dimensional graphene layer. The current \( j(t) = j^{(1)}(t) + j^{(3)}(t) \) in graphene has the linear and the third-harmonic components, \( j^{(1)}(t) = \sigma^{(1)}(\omega)E_\omega e^{-i\omega t} \) and \( j^{(3)}(t) = \sigma^{(3)}_{xxxx}(\omega, \omega, \omega)E_\omega^3 e^{-i3\omega t} \), where \( E_\omega \equiv E_{\omega, z=0} \) is the Fourier component of the self-consistent electric field at the plane \( z = 0 \), and \( \sigma^{(1)} \) and \( \sigma^{(3)} \) are the first- and third-order conductivities of an isolated graphene layer.

We solve the outlined nonlinear electrodynamic problem in two steps. First, we calculate, within the first-order response theory, Refs. \([\text{22} \text{ [27]}\)\], the \( \omega \) Fourier components of the electric field and current, and relate the amplitude of the ac electric field \( E_{\omega, z=0} \) at the plane \( z = 0 \) to the amplitude of the incident wave \( E_0 \). Then we substitute the third-order current \( j_{3\omega} = \sigma^{(3)}_{xxxx}(\omega, \omega, \omega)E_\omega^3 \) in Maxwell equations and calculate the amplitudes of the 3\( \omega \) Fourier components of the waves emitted in the forward and backward directions. We neglect the influence of the nonlinear effects on the amplitudes of \( E_{\omega, z=0} \); these effects, determined by \( \sigma^{(3)}_{xxxx}(\omega, \omega, -\omega) \), give small cor-
integer \( m \) as a function of \( d \) thickness from graphene lying on the dielectric substrate. In this case the third harmonic intensity \( I_{3\omega}(d)/I_{3\omega}(0) \) is the intensity of the third harmonic emitted in the backward (forward) direction, as a function of the dielectric thickness \( d \), at different metal thicknesses \( d_{Au} \), in the structure shown in the inset to Fig. 3(b). The wavelength of the incident radiation is \( \lambda_\omega = 10 \mu m \).

The dielectric slab,

\[
d = \frac{\lambda_\omega}{2n_1} m, \quad m = 0, 1, 2 \ldots
\]  

under these conditions the field \( E_\omega \) at \( z = 0 \) is maximal. In the maxima the values of \( I_{3\omega}(d) \) are the same as in the isolated graphene \( I_{3\omega}(0) \), but in the minima they can be several orders of magnitude smaller \( [I_{3\omega}(d)]/I_{3\omega}(0) \lesssim 10^{-3} \) in Fig. 1 here \( I_{3\omega}(0) \) is the third-harmonic intensity emitted only in one, forward or backward, direction. A proper choice of the dielectric thickness is thus of extreme importance for observation of the third harmonic generation. In Fig. 1 one also sees a difference in the intensity of the 3\( \omega \)-waves emitted in the forward and backward directions: the intensity of the backward radiation is smaller and has additional resonances corresponding to the interference condition for the third harmonic, \( d \simeq (\lambda_{3\omega}/2n_1)m, m = 0, 1, 2, \ldots \).

Now consider the case when a thin metallic (Au) layer with the thickness \( d_{Au} \) covers the backside of the dielectric substrate. In this case the third harmonic intensity strongly depends on whether the 3\( \omega \)-wave is emitted in the forward (transmission) or in the backward (reflection) direction. Figure 2 shows the normalized intensity of the third harmonic, emitted by the structure in the forward direction, as a function of the dielectric thickness \( d \) at several different metal thicknesses \( d_{Au} \).

A few interesting features are seen in Fig. 2. First, when the metal thickness \( d_{Au} \) increases from \( d_{Au} = 0 \) nm (the black solid curve; corresponds to the red dashed curve in Fig. 1) up to \( d_{Au} \simeq 5 \) nm, the maxima of \( I_{3\omega} \)
and the intensity $I_{3\omega}$ of the transmitted third-harmonic signal substantially (by more than one order of magnitude) increases. The quarter-wavelength shift in (3), as compared to (2), results from the boundary condition for the tangential electric field at the metallic plane $z = d$, $E_{z,z=0} \approx 0$. This also leads to a larger fundamental-frequency electric field $E_{z,z=0}$ at the graphene plane $z = 0$, and hence, to a larger third-harmonic signal.

When $d_{\text{Au}}$ grows further, the intensity $I_{3\omega}$ reaches its maximum and then decreases (at $d_{\text{Au}} \gtrsim 5$ nm), since at large $d_{\text{Au}}$ the metal layer becomes opaque both for the fundamental ($\omega$) and for the third ($3\omega$) harmonic. But since the $3\omega$-waves are reflected from the graphene, $D = $ dielectric, $M = $ metal. The wavelength of the incident radiation is $\lambda_{\omega} = 10$ μm.

Figure 3 shows the intensity of the third harmonic emitted in the backward direction. One sees that the maxima of the curves $I_{3\omega}(d)$ also move to the $d$-values when $d_{\text{Au}}$ increases. However, in contrast to the forward-direction emission, in these $d$-points $I_{3\omega}$ monotonously grows with $d_{\text{Au}}$ and saturates at $d_{\text{Au}} \gtrsim 100$ nm, reaching the value $I_{3\omega}(d)/I_{3\omega}(0) \approx 226$. If to take into account that the total third-harmonic intensity emitted by an isolated graphene layer in both (forward and backward) directions equals $2I_{3\omega}(0)$, one sees that just the metalization of the backside of the substrate may increase the total emitted $3\omega$ power by more than two orders of magnitude (by the factor of $\approx 113$).

Such a giant enhancement of the third harmonic intensity is explained by the interference of both the incident wave ($\omega$) and its third harmonic ($3\omega$) in the dielectric slab. Indeed, in the case of a single (isolated) graphene layer in air the third-order current in the layer is of order $|j_{3\omega}| \approx \sigma(3)E_{\omega}^{3}$ when $d_{\text{Au}} \gg 0$, where $E_{0}$ is the amplitude of the incident wave (in this simple estimate we ignore the difference between $E_{\omega,z=0}$ and $E_{0}$). The electric and magnetic fields of the emitted third harmonic are proportional to $j_{3\omega}, E_{3\omega} \propto H_{3\omega} \propto \sigma(3)E_{0}^{3}$, and the intensity of the emitted radiation (in one direction) is proportional to $|E_{3\omega}|^{2}$. The total emitted power (both in the backward and forward directions) is then $I_{3\omega}^{\text{single layer}} \approx 2|\sigma(3)E_{0}^{3}|^{2}$.

If the graphene layer lies on the dielectric slab metalized on the back side, the fundamental-frequency electric field at the plane $z = 0$ is twice as large (in the interference maximum) as the incident wave field, $E_{\omega,z=0} \approx 2E_{0}$, due to the reflection of the wave from the back-side mirror. The third-order current is then $j_{3\omega} \approx \sigma(3)E_{\omega,z=0} \approx 2\beta\sigma(3)E_{0}^{3}$. The fields $E_{3\omega}, H_{3\omega}$ of the excited third-harmonic wave, emitted from the graphene plane $z = 0$ in both directions, are proportional to the current $j_{3\omega}$, but since the $3\omega$-wave is reflected from the mirror again, they should be multiplied by two once more, $E_{3\omega} \propto H_{3\omega} \propto 2j_{3\omega} \propto 2^{4}\sigma(3)E_{0}^{3}$. The total emitted power (only in the backward direction) is then proportional to $I_{3\omega}^{\text{single layer}} \approx 2^{8}|\sigma(3)E_{0}^{3}|^{2}$. Comparing $I_{3\omega}^{\text{single layer}}$ with the value $I_{3\omega}(0)$, we see that the amplification factor, due to the substrate with a metalized back side, is about $2^{7} = 128$. The slightly smaller factor $\approx 113$ obtained in the more accurate theory above (Fig. 3) is due to the small difference between $E_{\omega,z=0}$ and $E_{0}$ which we have neglected.

Our results thus show that, placing graphene on the surface of a dielectric slab with a metalized back side one can increase the generated third-harmonic intensity by more than two orders of magnitude (a further enhancement of the third harmonic can be achieved by placing graphene inside a Fabry-Pérot-type cavity with a high quality factor). Parameters of such a graphene-based frequency multiplier should however be carefully chosen since the dielectric thickness $d$ and the input radiation frequency $\omega$ (or the wavelength $\lambda_{\omega}$) should be related by the resonant conditions (3). As seen from Figs. 4 – 6 deviations from these relations may suppress the output $3\omega$ signal by orders of magnitude. In addition, a further (resonant) enhancement of the third harmonic at infrared
frequencies can be achieved by tuning the density of electrons $n_e$ in graphene, since the positions of the inter-band resonances depend on the Fermi energy.

It should be noticed that numerical values of the third-order parameters of graphene, experimentally measured in different papers, quite substantially differ from each other, see, e.g., a discussion in [19]. This may be due to a better or worse fulfillment of the resonant conditions in (2) or (3) in different experiments. It can also be noticed that another way to increase the third harmonic generation effect in the structure graphene–dielectric–metal and found the optimal operation conditions of such a frequency multiplier, Eq. (3). Properly choosing the system parameters one can get a giant, resonant enhancement of the up-conversion efficiency. Conversely, under the off-resonant conditions the device efficiency is suppressed by many orders of magnitude. The correct choice of the device parameters, Eq. (3), is of particular importance for its proper operation.

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