Planar tetra-coordinate carbon resulting in enhanced third-order nonlinear optical response of metal-terminated graphene nanoribbons

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1. The detailed equations used for the calculation of nonlinear reflectivity

The nonlinear reflectivity \( R \) can be expressed as:

\[
R = \tan^2 \left[ | \gamma' | I \right] \quad (1)
\]

Where \( I \) is the length of devise (0.2cm is used in this study); \( \gamma' \) is coupling coefficient which can be written as:

\[
\gamma' = \frac{\omega}{2cn_0(\omega)} \chi^{(3)} A^2 \quad (2)
\]

Here, \( \omega \), \( n_0 \) and \( A \) are frequency, refractive index and real amplitude functions of plane pump waves, respectively. The power of laser is related to \( A \):

\[
I = \frac{1}{2} \varepsilon_0 n_0(\omega)cA^2 \quad (3)
\]
In this paper, we set $I=10^{12}\text{w.m}^{-2}$. Third-order optical susceptibilities $\chi^{(3)}$ of bulk materials can be estimated from the average third-order polarizability $<\gamma>$:

$$\chi^{(3)}(-\omega_p;\omega_1,\omega_2,\omega_3) = N f(\omega_1)f(\omega_2)f(\omega_3) <\gamma> \quad (4)$$

and the local field factor $f(\omega_i)$ is expressed as:

$$f(\omega_i) = [n(\omega_i)^2 + 2]/3 = 1/[1 - (4\pi/3)N\alpha(\omega_i)] \quad (5)$$

where $f(\omega_i)$ is at radiation frequency $\omega_i$, $N$ is the dimmer number density (The distance between GNRs is about 0.34nm. According to the size of studied materials, we set the $N$ to be $1.56 \times 10^{27}\text{m}^{-3}$), and $n(\omega_i)$ and $\alpha(\omega_i)$ are the refractive index and the polarizability, respectively, and can also be obtained by the TDDFT-SOS method.

After the $n(\omega_i)$, $A$, and $\chi^{(3)}(-\omega_p;\omega_1,\omega_2,\omega_3)$ have been calculated, we will obtain the dynamic (under different input photon energy $h\omega_i$) nonlinear reflectivity $R$.

2. Supporting figures
**Figure S1.** The dynamic third order NLO polarizabilities (polarizabilities under different input photon energy) for THG process.

![Graphs showing dynamic third order NLO polarizabilities for different input photon energies and samples.](image)

**Figure S2.** The dynamic third order NLO polarizabilities (polarizabilities under different input photon energy) for DFWM process.

![Graphs showing dynamic third order NLO polarizabilities for different input photon energies and samples.](image)
**Figure S3.** Dynamic nonlinear reflectivity (R value under different input photon energy) of (a) (7, 3) Cu-ZGNR, (b) (3, 7) B-AGNR, (c) (3, 7) Be-AGNR and (d) (3, 7) H-AGNR.

**Figure S4.** The orbital configurations of the most contributed states as described in Table 2. (a) H-5 of (7, 3) Cu-ZGNR, (b) L+7 of (7, 3) Cu-ZGNR, (c) H of (3, 7) B-AGNR, (d) L+16 of (3, 7) B-AGNR (e) H-7 of (3, 7) Be-AGNR, (f) L+1 of (3, 7)
Be-AGNR, (g) H-1 of (3, 7) H-AGNR, and (h) L+7 of (3, 7) H-AGNR.

**Figure S5.** Frequency-dependent TPA cross sections of Be-AGNRs.

**Figure S6.** The relationship of $\text{Im} \gamma(-\omega;\omega,\omega, -\omega)$ versus two-photon states at the resonant energy for Be-AGNRs.