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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:

$$R = \tan^2[|\gamma'|l] \quad (1)$$

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

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

Here, ω, 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:

$$I = \frac{1}{2}\varepsilon_0 n_0(\omega) c A^2 \quad (3)$$

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

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

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 ω_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 1.56×10^{27}m^{-3}), and n(ω_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(ω_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 $\hbar\omega_i$) nonlinear reflectivity R.

2. Supporting figures

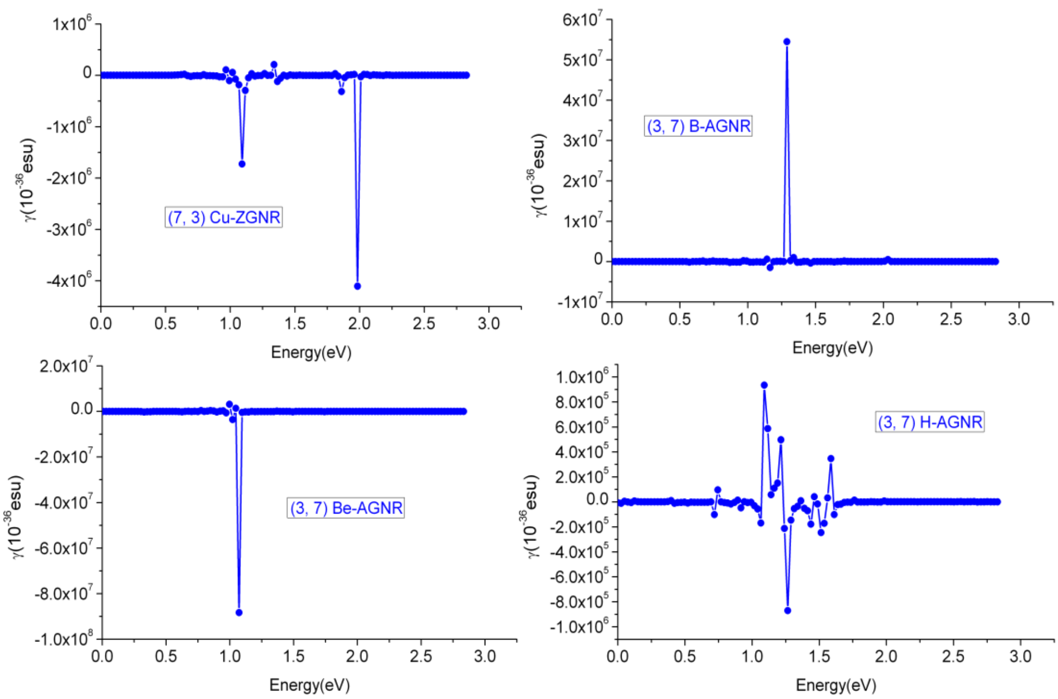

Figure S1. The dynamic third order NLO polarizabilities (polarizabilities under different input photon energy) for THG process.

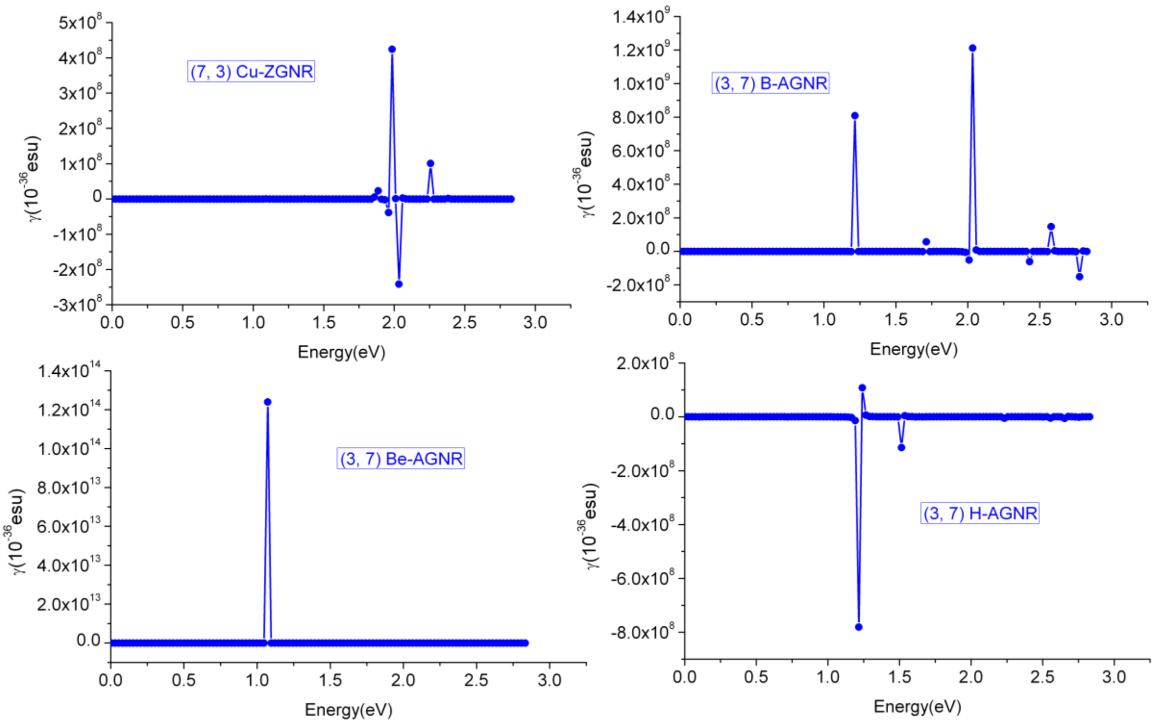

Figure S2. The dynamic third order NLO polarizabilities (polarizabilities under different input photon energy) for DFWM process.

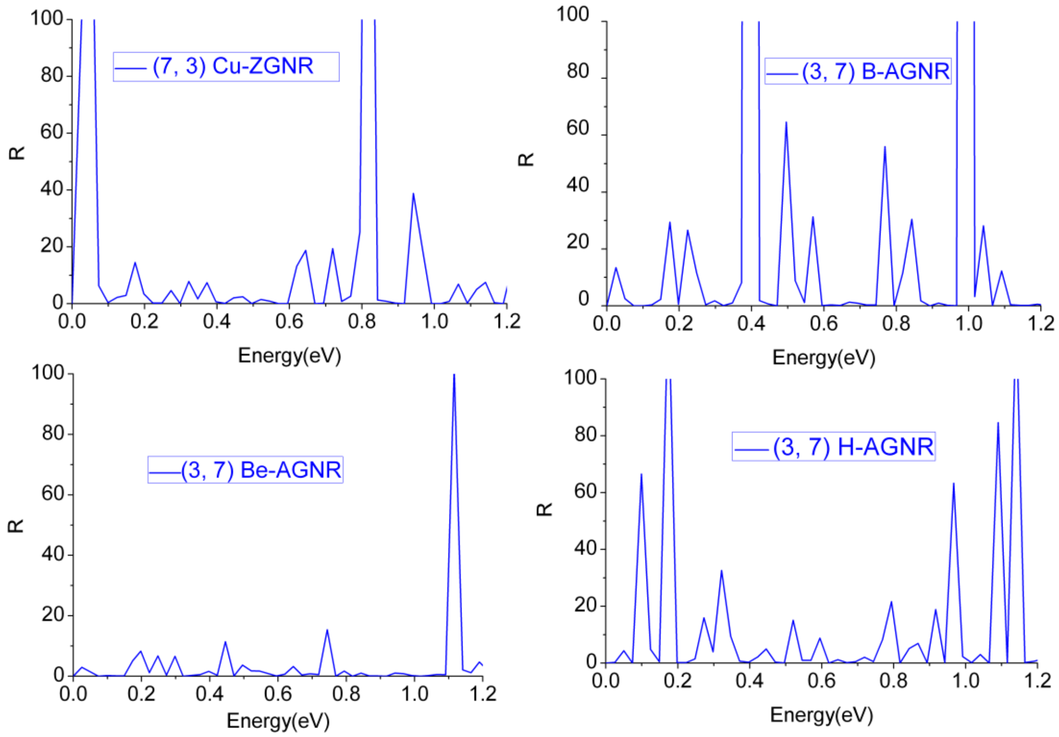

Figure S3. Dynamic nonlinear reflectivity (R value under different input photon energy) of (a) (7, 3) Cu-ZGNR, (b) (3, 7) B-AGNR, (c) (3, 7) Be-AGNR and (d) (3, 7) H-AGNR.

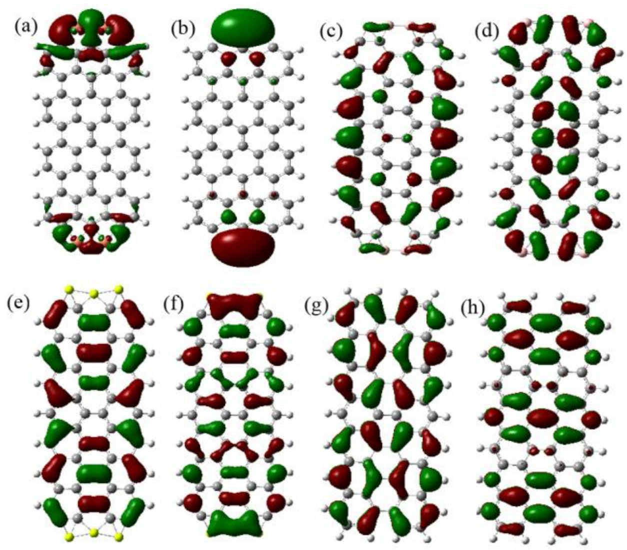

Figure S4. The orbital configurations of the most contributed states as described in Table 2. (a) H-5 of (7, 3) Cu-ZGNR, (b) L+7 of (7, 3) Cu-ZGNR, (c) H of (3, 7) B-AGNR, (d) L+16 of (3, 7) B-AGNR (e) H-7 of (3, 7) Be-AGNR, (f) L+1 of (3, 7)

Be-AGNR, (g) H-1 of (3, 7) H-AGNR, and (h) L+7 of (3, 7) H-AGNR.

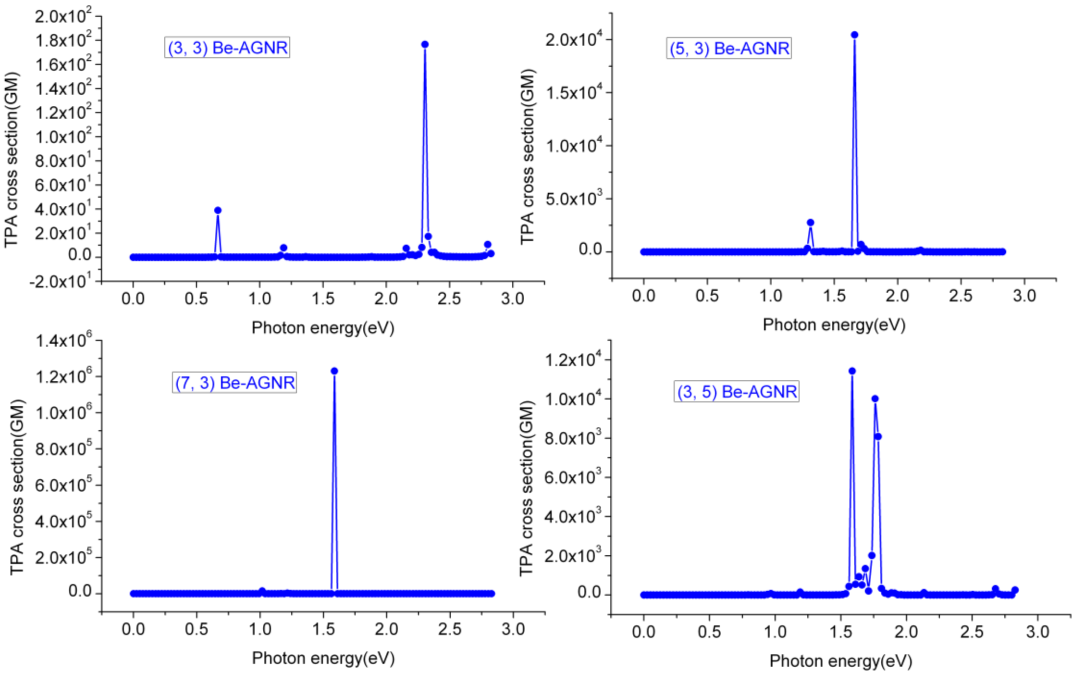

Figure S5. Frequency-dependent TPA cross sections of Be-AGNRs.

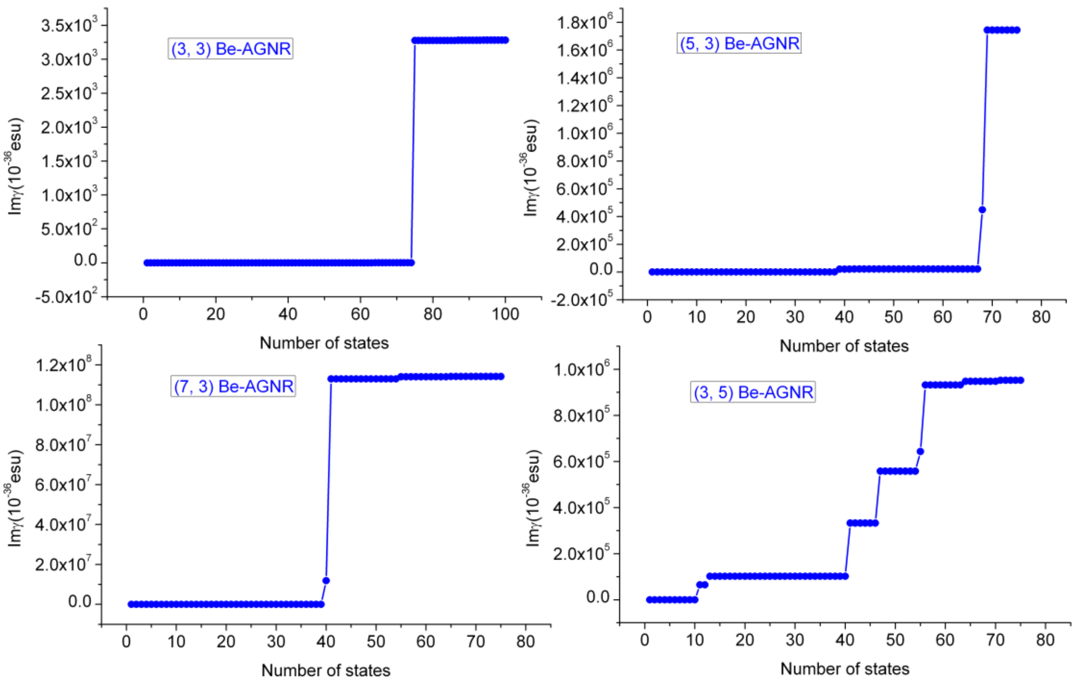

Figure S6. The relationship of Imγ(-ω;ω,ω, -ω) versus two-photon states at the resonant energy for Be-AGNRs.