Graphene Plasmonics



Approaching the Intrinsic Lifetime and Modulating a Graphene Plasmonic Resonance at a Few Hundred GHz

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Graphene-based metamaterials exhibit large tunability, low insertion loss, and high field confinement compared with metal-based structures. Graphene-based metamaterials may find numerous applications in optical modulators, optoelectronic devices, and chemical sensors in the few-hundred-GHz and low-THz regime, constituting a new frontier as electronics and wireless communication continuously push further to higher frequencies. However, the main challenge is overcoming loss in graphene-based resonant applications. Here, a low-loss graphene plasmonic resonant modulator is demonstrated that operates at a few hundred GHz and 1 THz. The modulation depth is in excess of 35% with two layers of graphene. Numerical simulations show good agreement with the experimental results and reveal 100-200 fs lifetimes, which are approaching the intrinsic lifetime of the graphene plasmon due to the suppression of loss from phonon and edge scattering. The above values are the closest to electronic frequencies and represent the longest plasmon lifetime and largest modulation depth in graphene plasmon resonance devices reported so far.

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Surface plasmons describe collective oscillations of electrons in metals or semiconductors.^[1] Generally, surface plasmons can exist in any material with free charge carriers whose response to an electric field is reactive, that is, whose complex conductivity is predominantly imaginary.^[2] Plasmons in graphene are collective excitations of 2D massless electrons, which can tightly confine electromagnetic waves at a subwavelength scale with a longer excitation lifetime than plasmons in metals.^[3-5] Moreover, unlike surface plasmons in metals or semiconductors, plasmons in graphene can be effectively tuned with an electrical gating. The tunability of the charge carriers in graphene $(10^{13}-10^{14} \text{ cm}^{-2})^{[6]}$ is an order of magnitude larger than that of conventional 2D electron gas systems.^[7,8] These unique characteristics of graphene plasmons enable a broad range of applications, such as photodetectors,^[3] plas-

monic sensors,^[4,9] tunable plasmonic waveguides,^[10] and potentially optoelectronic applications in the few-hundred-GHz and low-THz frequency range.^[11,12] To excite graphene plasmons with electromagnetic radiation, various approaches have been proposed, including light scattering by a near-field subwavelength structure such as a sharp metal tip,^[2,13] coupling by a grating fabricated below or on top of a graphene sheet,^[14-16] or patterning graphene to form plasmonic metamaterials (e.g., ribbons, disks, and an antidot array) as cavities for localized surface plasmon polaritons.^[4,5,7,9,11,17] The last approach is both simple and flexible in light of modern micro/nanofabrication techniques that allow engineering graphene into a multitude of graphene metamaterials. However, the main drawback of graphene plasmonic devices is their high loss. Previously reported graphene plasmon lifetimes are in the range of 15-85 fs in the literature, [14,16,18,19] which represent the inverse of the loss over time. All of these investigations were concentrated in the infrared range (100–2000 cm^{-1} or 3.3–60 THz), and few or no studies have reported resonant features of graphene plasmons in a frequency range below 3 THz. Meanwhile, the imaginary part of the permittivity of graphene will increase quickly with a reduced optical frequency below THz frequencies, which makes the loss problem seems even worse in the fewhundred-GHz or low-THz regime.



Here, we report the first study of tunable plasmon excitations in the 0.1-2.5 THz range with complementary-pattern graphene metamaterials, namely, a graphene complementary split-ring resonator (GCSRR) array. The results show a resonance peak with a center frequency of 0.7 or 1 THz for two different polarization settings. With the tuning of the gate voltage, the modulation depth of the peak can be over 35% with two layers of graphene. By fitting between the simulation and experimental data, we obtain a plasmon lifetime of 200 fs for the 0.7 THz resonance frequency and 100 fs for the 1 THz resonance frequency. This long lifetime is much longer than the previously reported few tens of femtoseconds at infrared frequencies and is the result of disabling optical phonon scattering and suppressing edge scattering, thus approaching the intrinsic lifetime, which is the lifetime only due to carrier transitions, of the graphene plasmon. So far, our results represent the lowest frequencies, i.e., those closest to electronic frequencies, the highest modulation depth. and the longest lifetime reported in graphene plasmon resonance devices. At the same time, our device functions as a THz frequency-selective modulator or a mixer, which may enable graphene few-hundred-

GHz optoelectronic applications. Our results further demonstrate the feasibility of graphene plasmon resonances in the few-hundred-GHz to THz region and may inspire new applications.

In this work, we focus on a GCSRR structure because this structure can be more readily excited by low-frequency THz waves than other structures (e.g., antidots and antiribbons, see the Supporting Information). To excite plasmonic resonances in graphene, we have to tailor the graphene sheets into subwavelength structures. To achieve good tunability and reliability, the structures are usually designed as a network form, namely, a complementary style, such as antidots or antiribbons.^[4,7,11] To effectively resonate with waves in the THz regime, the unit dimensions of the graphene metamaterials should be engineered to tens of micrometers. Thus, a large area of the graphene sheet has to be etched for normal patterns, e.g., antidots or antistrips. In contrast, the GCSRR structure can greatly maintain the area coverage of graphene, as its resonance frequency is mainly determined by the circular length of the split ring, and its line width can be very narrow. The designed GCSRR structure is shown in Figure 1a, and its unit sizes and parameters are as follows: array period lengths in the *x*, *y* directions, $P_x = 24 \mu m$, P_y = 43 µm; split-ring resonator (SRR) unit lengths in the *x*, *y* directions, $L_x = 21 \ \mu\text{m}$, $L_y = 40 \ \mu\text{m}$; SRR gap size, $G = 5 \ \mu\text{m}$; and the SRR line width, $W = 2 \mu m$.

Monolayer graphene was grown by chemical vapor deposition and then transferred onto a high-resistivity SiO₂/Si



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Figure 1. Schematics of the device and experiment. a) Schematic of the GCSRR array structure ($P_x = 24 \,\mu\text{m}$, $P_y = 43 \,\mu\text{m}$, $L_x = 21 \,\mu\text{m}$, $L_y = 40 \,\mu\text{m}$, $G = 5 \,\mu\text{m}$, and $W = 2 \,\mu\text{m}$). b) Fabrication process of the graphene plasmonic modulator made up of the GCSRR-array/ionic-liquid/GCSRR-array sandwich structure. The substrates are SiO₂/Si wafers. c) 3D schematic representation of the experimental setup for the THz transmission measurement at various gate voltages. The four electrode contacts on each graphene sheet are used together during the measurements, but for simplicity, only two contacts are connected in the graph.

substrate. Four Au/Cr electrodes were deposited on the corners of a $6 \times 6 \text{ mm}^2$ graphene sheet with a shadow mask in a vacuum environment. The GCSRR arrays were implemented at the center of the graphene sheet by standard UV photolithography and oxygen plasma etching. Finally, a wet chemical approach (chloroform cleaning and subsequent 2-propanol rinsing)^[20] was performed to remove chemical residues on the patterned graphene. For the assembled device, we adopted a graphene/ionic-liquid/graphene sandwich structure, which was fabricated by stacking two graphene GCSRR metamaterials face to face with a spacer and a layer of ionic liquid injected in between (Figure 1b), to maximize the modulation depth. The structure orientations of the two GCSRR arrays are aligned in the same orientation to avoid resonance peak broadening. As shown in Figure 1b, two bracket-shaped spacers (≈50 µm thick) surround the GCSRR arrays at the center of the two graphene sheets and form a cavity to hold the ionic liquid. Figure 1c shows an application configuration of a frequency-selective modulator device, which is also the simplified experimental setting for voltagebiased THz transmission measurements. For simplification, only two electrodes of the graphene sheets were connected to the voltage source in the schematic. In the actual measurements, all eight electrodes were employed with the gate voltage to produce the best gating effect.

Preliminary characterizations are carried out to evaluate the quality of the fabricated devices. **Figure 2**a shows a typical scanning electron microscopy (SEM) image of the





Figure 2. Characterizations of graphene plasmonic devices. a) A typical SEM image of the GCSRR structure. The GCSRR array (6 mm × 6 mm) is fabricated with transferred large-area chemical vapor deposition (CVD) graphene through UV photolithography and oxygen plasma etching. b) Raman spectrum of the patterned graphene, manifesting the signature Raman peaks of monolayer graphene with a low defect density. c) Experimental setup of the transport measurements in a field-effect transistor configuration. d) Gate-dependent source–drain resistance of a GCSRR structure, measured under the configuration shown in (c). The orange and yellow curves are for the gate voltage (V_g) upward scan and downward scan, respectively. Both curves indicate the charge neutrality point, V_{CNP} , at ≈0.5 V, with a deviation of ≈0.2 V, which may stem from the hysteresis effect caused by charge traps.

GCSRR structures. The signature Raman peaks in Figure 2b demonstrate that the patterned graphene is a high-quality monolayer. The electrical properties of the patterned graphene sheets are characterized by measuring the sourcedrain resistance of the finalized devices as a function of the gate voltage. The device's electrode layout and circuit connections are illustrated in Figure 2c. The result of a device is plotted in Figure 2d. The graphene sheet is found to be naturally hole-doped, and the charge neutrality point is achieved when the gate voltage is ≈ 0.5 V (±0.1). The V_{g} downward scan curve slightly deviates from the upward scan curve, and this hysteretic behavior may be caused by charge traps or a delayed response in the graphene sheet.^[14] The sourcedrain resistance shows a strong modulation in response to a change in gate voltage. This is the result of carrier concentration changes in the GCSRR array layers, between which ionic liquid allows a large doping range through electrostatic gating.^[21] Moreover, the sandwich structure employs the ionic liquid simultaneously in both graphene layers and makes use of the high mobility of the electrons and holes in the two layers, further enhancing the modulation depth.

By applying gate voltages to the two patterned graphene films, the Fermi level, and hence the carrier concentration, can be effectively modulated with a corresponding change in conductivity. This modified conductivity leads to variations in the complex permittivity of the engineered graphene structure, which will result in changes in the transmitted THz waves.

To study the carrier-density-dependent resonance characteristics of the fabricated graphene devices, transmission spectra are measured at various voltage biases with a THz time-domain spectroscopy (THz-TDS) system^[22] in the frequency range of 0.1-3 THz (3.3-100 cm⁻¹). Linear polarized THz waves are generated by a photoconductive antenna and detected by a ZnTe (110) crystal. The THz transmission measurements are performed in a nitrogen-purged chamber at room temperature. Figure 3 summarizes the transmitted THz spectra and normalized spectra of the graphene plasmonic device excited by THz waves with parallel or perpendicular polarizations (relative to the split-ring gap direction, as shown in the insets). For clear viewing, we only plot the positive voltage bias data in Figure 3. The transmission spectra at negative gate voltages have similar behaviors and are provided in the Supporting Information.

Gate-dependent transmission spectra for THz waves polarized parallel or perpendicular to the SRR gap direction is shown in Figure 3a,b, respectively. As the gate voltage moves away from the charge neutrality point ($V_{CNP} = 0.5$ V), the transmitted electrical field decreases monotonically. This result demonstrates an effective modulation of the carrier





Figure 3. Control of plasmon resonances by an electrical gating. a,b) Gate-induced change in the transmission spectra with incident THz radiation polarized parallel (a) and perpendicular (b) to the orientation of the split-ring gap. c,d) Normalized THz transmission spectra $(T/T_{CNP})^2$ at different gate biases for parallel (c) and perpendicular (d) polarizations. The curves' corresponding gate voltages are labeled as legends in (a) and (b) and as text on top of the curves in (c) and (d).

concentration. It is noteworthy that the amplitude of the THz electrical field changes unevenly in different frequency regions, indicating resonance characteristics. Plasmonic resonances in the GCSRR arrays constitute the underlying physics and are also tuned in situ by electrostatic doping. This resonant behavior is much clearer and better illustrated in Figure 3c,d after normalization of the spectrum at the charge neutrality point.

To gain clear insight into the plasmonic resonances, Figure 3c,d plot the power transmission spectra normalized by the spectrum at the charge neutrality point, $(T/T_{CNP})^2$. For incident light polarized parallel to the SRR gap direction (in Figure 3c), prominent plasmon absorption peaks are observed at ≈1 THz, where the oscillation gains strength with an increased carrier concentration. For incident light polarized perpendicular to the SRR gap direction (in Figure 3d), the plasmonic resonances respond to the gating change in a similar way, but with absorption peaks at 0.7 THz (in Figure 3d). The difference in the resonance frequency between the two polarizations is due to the different modes of an asymmetric resonator.^[23] A simpler and approximate view is that the length difference in the two directions gives different resonance frequencies. A larger feature size will give a lower resonance frequency, which is why the perpendicular wave has a lower center frequency than the parallel polarized wave. The two different center frequencies also prove that the curves in Figure 3c,d are indeed GCSRR feature-sizedependent plasmon resonance peaks. The modulation depths in the intensity for both polarizations exceed 35%, which is the highest modulation ratio among homogeneous graphene metamaterials to date.^[7,11] This is the result of passing only two layers of graphene, and the modulation depths should be stackable and enhanced with multiple devices working in series.

THz modulators are of great interest to the research community,^[24-30] and it is worth mentioning that this device can be regarded as a fixed-frequency-selective modulator. The shifting of the center frequency is only $\approx 10\%$ as the amplitude modulation happens and is much smaller than the width of the peak. The resonance frequency, $\omega_{
m sp}$, of a graphene plasmon device depends on the carrier density and the size of the device $(\omega_{sp} \propto W^{-\frac{1}{2}}n^{\frac{1}{4}})$,^[7,11] where W is the dimension of the graphene structure unit, and n is the carrier density. In previous reported studies, the typical dimensions of the graphene structures were only several micrometers^[4,7,11] and showed significant (larger than 1/3 of the center frequency) frequency shifting as the carrier density changed. Here, our GCSRR devices have a unit length of 20-50 μ m, which is a much larger W and produces very little change in ω_{sp} when the gating modulates the resonance amplitude. This feature of our device enables frequency-selective modulation, which is an important ability in selective channel modulation in frequencydivision multiplexed signals.

Moreover, our device is also an optoelectronic mixer working at a few hundred GHz. A mixer working at such a high frequency is rare because most nonlinear semiconductor devices fail at this high frequency. The inputs are a





Figure 4. Simulated electromagnetic (EM) field and normalized transmission spectra. a,b) Simulated z (into paper) direction of the magnetic field of the GCSRR under parallel (a) and perpendicular (b) polarized excitations. The color maps represent the profile of the strength of the magnetic field. The red arrows represent the current flow directions. The black axes represent the field settings of the incident electromagnetic waves. c,d) Simulated and fitted experimental transmission spectra for parallel (c) and perpendicular (d) polarized excitations. For the simulation, the carrier density is set as 1.5×10^{13} cm⁻²; the relaxation time is set as 100 fs for the parallel polarization and 200 fs for the perpendicular polarization. The experimental spectra are the spectra for a gate voltage of 2.5 V in Figure 3c,d.

high-frequency optical signal and a low-frequency electrical signal,^[31] the output signals are an amplitude-modulated high-frequency signal or a carrier-mixed low-frequency signal, both in optical or electrical format. Here, in our experiment, we only measured and demonstrated the optical output signal. The mixed electrical signal should be in the graphene device as well, as our simulation shows in the next paragraph. To the best of our knowledge, 0.7 THz is the lowest resonance frequency for graphene plasmons reported in the literature, arrives at the frequency range of a few hundred GHz, and is addressable and transmittable by both optical and electronic methods. This work proves the potential and enables the possibility of graphene plasmons for few-hundred-GHz optoelectronic devices.

To gain deep insight into graphene plasmons, electromagnetic field profiles and resonance curves are calculated for the two plasmonic resonance modes using finite-element frequency domain methods.^[11,14] In our numerical calculations, the graphene film is modeled as a homogeneous medium and described by its dielectric function of graphene, $\varepsilon_r(\omega)$, which is a function of the frequency ω . $\varepsilon_r(\omega)$ is further calculated from the complex conductivity $\sigma(\omega)$ as $\varepsilon_r(\omega) = \frac{i\sigma(\omega)}{\omega\varepsilon_0 t_g}$, where ε_0 is the permittivity of vacuum, and t_g is the thickness of graphene (set as 1 nm, which is sufficiently thin to reach a good convergence^[15]). The complex conductivity of graphene is calculated within the local random phase approximation $(\text{RPA})^{[15,32]}$ as

$$\sigma(\omega) = \frac{2e^2\omega_{\tau}}{\pi\hbar} \frac{i}{\omega + i\tau^{-1}} \log\left[2\cosh\left(\frac{\omega_{F}}{2\omega_{\tau}}\right)\right] + \frac{e^2}{4\hbar} \left[H\left(\frac{\omega}{2}\right) + i\frac{2\omega}{\pi}\int_{0}^{\infty} \frac{H\left(\frac{\omega}{2}\right) - H\left(\frac{\omega}{2}\right)}{\omega^2 - \omega^2} d\omega'\right],$$

where $H(\omega) = \frac{\sinh\left(\frac{\omega}{\omega_{T}}\right)}{\cosh\left(\frac{\omega_{F}}{\omega_{T}}\right) + \cosh\left(\frac{\omega}{\omega_{T}}\right)}, \quad \omega_{F} = \frac{E_{F}}{\hbar}, \quad \omega_{T} = \frac{k_{B}T}{\hbar}, \text{ and}$

 $E_F = \hbar v_F \sqrt{\pi n_{2D}}$. ω is the frequency of the incident light, τ is the relaxation time of the carriers or the lifetime of the plasmon, $E_{\rm F}$ is the Fermi level, $v_{\rm F}$ is the Fermi velocity (set as 10^6 m s^{-1}), n_{2D} is the electron density, \hbar is the reduced Planck constant, $k_{\rm B}$ is the Boltzmann constant, and T is the temperature set at 300 K. The first term of the equation represents the contribution of the free carriers (intraband transitions), and the second term describes the contribution of interband transitions.^[15] Applying a gate voltage changes the carrier density and the complex permittivity of graphene, thus modulating the transmission of the THz waves. Figure 4a,b show the calculated magnetic field profiles of the GCSRR arrays under parallel and perpendicular polarized excitations, respectively. For the incident light polarized parallel to the SRR gap orientation, the magnetic field mainly concentrates at the gap and the bottom of the GCSRR unit, and two counterpropagating

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currents are produced at the gap (the flow directions are indicated by the red arrows). This mode acts like a resonant LC circuit, so it can be regarded as an LC mode. For incident light polarized perpendicular to the SRR gap orientation, the magnetic field mainly concentrates at the two lateral sides of the GCSRR unit, and two lateral currents flow in the same direction. This resonance mode behaves like an electromagnetic dipole, so it is termed a dipole mode.^[16,33] Figure 4c,d show the simulated normalized THz transmission spectra in comparison with the experimental results at a gate voltage of 2.5 V shown in Figure 3c,d. The simulated spectra exhibit good agreement with the experimental data and allow us to estimate the carrier concentration of graphene, which is 1.5×10^{13} cm⁻² (at 2.5 V), corresponding to a Fermi level of \approx 0.45 eV. The oscillations in the simulated curves near the right edges of Figure 4c,d show mismatches with the experimental data, are false signals due to limited calculation boundaries in the time domain and originate from the Fourier transformation of the long-duration signal. In addition, we can also obtain the value of τ , the relaxation time of the carriers or the lifetime of the plasmon resonances, which is 100 fs for a 1 THz resonance or 200 fs for a 0.7 THz resonance, respectively.

Here, at a THz frequency, the lifetime of the plasmon resonance can be mathematically treated as the relaxation time of the carriers, although it probably includes both background damping due to impurities and additional damping due to acoustic phonon scattering. In general, the lifetime of a plasmon resonance in graphene is $\tau_{\rm pl} = (\tau^{-1} + a/W_{\rm e} + \tau_{\rm ep}^{-1})^{-1}$, where τ is the relaxation time of the carriers and describes a background damping due to scattering with impurities, a/W_{e} is related to scattering at the edges, and $\tau_{\rm ep}$ is the plasmon lifetime due to scattering with phonons.^[18] τ was considered to be 85 fs in previously reported work,^[18,19] close to our result of 100-200 fs. The term a/W_e is at least an order of magnitude smaller than τ^{-1} , because $a \approx 2 \times 10^6 \text{ ms}^{-1}$ and W_e is larger than 20 μ m. τ_{ep} is the lifetime due to electron-phonon coupling and generally should include scattering both from optical and acoustic phonons. Optical phonon scattering should be much larger than acoustic phonon scattering and is only considered at midinfrared frequencies where the plasmon energy is large enough to enable optical phonon scattering.^[18] However, at THz frequencies, the plasmon energy is too small to enable optical phonon scattering, and au_{ep} only includes acoustic phonon scattering. Therefore, plasmon damping at THz frequencies is mainly controlled by scattering from impurities and acoustic phonons.

Our graphene plasmon resonance lifetime is much longer than previously reported lifetimes from graphene devices and is improved by suppressing loss from optical phonon and edge scattering. For instance, tunable THz split-ring resonators have been reported for metal–graphene hybrid, middle infrared frequency, back-gated devices^[34] and U-shaped ~0.1 µm feature size on-SiC devices.^[35] In principle, metal–graphene hybrids are not comparable to pure graphene devices. If we have to compare, our ~1 THz resonance frequency is much smaller than the optical phonon frequencies (~1500 cm⁻¹) in graphene and the operating frequency (~3000 cm⁻¹) of the reported metal– graphene hybrid.^[34] At the same time, our device's feature size is at the scale of $\approx 10 \ \mu\text{m}$, which is much larger than the $\approx 0.1 \ \mu\text{m}$ feature size in on-SiC devices.^[35] As discussed in the previous paragraph, three terms (intrinsic scattering, phonon scattering, and edge scattering) control the graphene plasmon lifetime. Our design suppresses optical phonon scattering and edge scattering to a level that is smaller than the intrinsic scattering, thus improving the lifetime.

We believe that our value of 200 fs is probably the best one can achieve for a graphene plasmon on a SiO₂ substrate and is approaching the intrinsic lifetime-the lowest possible damping of a graphene plasmon at room temperature. A longer lifetime is very important in graphene devices, because a longer lifetime means less loss, which is a key issue in graphene plasmonic applications.^[36] The limitation or intrinsic lifetime for a graphene plasmon at room temperature should be ≈ 400 fs (or 600 fs at low temperature), which is estimated by $\tau = \mu E_{\rm F}/ev_{\rm F}^2$ for $E_{\rm F} = 0.1$ eV, where $v_{\rm F}$ is the Fermi velocity, with the best reported electron mobility $\mu \approx 40\ 000\ {\rm cm^{-2}\ V^{-1}\ s^{-1}}$ at room temperature (60 000 ${\rm cm^{-2}\ V^{-1}}$ s⁻¹ at 4 K) from DC transport measurements on single-crystal graphene on a boron nitride substrate.^[37] The lifetime at the 0.7 THz resonance is \approx 200 fs, which is already close to the limitation and is the same if the best electron mobility on a SiO₂ substrate is used to calculate the lifetime. The lifetimes of graphene plasmons here are much longer than previously reported experimental lifetimes (from 15 to 85 fs) in the literature,[14,16,18,19] because edge scattering is appreciably reduced and negligible and optical phonon scattering is disabled at THz frequencies, as we discussed in the previous paragraph. The lifetime at the 1 THz resonance is ≈ 100 fs. which is smaller than 200 fs at the 0.7 THz resonance, and this difference is probably due to increased acoustic phonon scattering with a higher plasmon energy. The best way to further reduce the damping or increase the lifetime is to replace the substrate with a single-crystal boron nitride wafer; however, single-crystal boron nitride larger than 1 cm in size has not been reported so far, and THz frequency devices need such large-size materials.

In summary, we studied the carrier density dependence of graphene plasmons in the low-frequency THz range, presented a graphene-based THz frequency-selective modulator, and achieved multiple records in graphene plasmonic devices. We demonstrated the lowest operating frequency (0.5–1 THz) achieved thus far, enabling few-hundred-GHz optoelectronic devices. We presented the longest plasmon lifetime and accordingly suppressed the loss, which is the key drawback of graphene plasmon devices, and showed the largest modulation depth in graphene plasmon resonance devices. These new steps may inspire new applications of graphene-based metamaterials, such as THz chemical/ biological sensors, THz switches, modulators, and filters, and may pave the way for applications of graphene in the few hundred GHz region.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.



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Conflict of Interest

The authors declare no conflict of interest.

Keywords

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