White Light from Nanothermometers

Thomas Prevenslik
QED Radiations, Berlin 10777, Germany

Abstract: Laser induced white light (WL) spectra of a graphene ceramic based on temperatures far less than Planck's theory of black-body radiation suggested the opening of a band-gap in graphene by multiphoton ionization. The difficulty is the WL spectra has nothing to do with graphene, but rather the WL spectra is emission of 30-150 nm Er^{+3} - Y2O3 nanoparticles (NPs) used as thermometers encrusted in the graphene to measure temperature. The Er^{+3} spectra is shown to closely match that of the measured graphene ceramic spectra. Even so, the Er^{+3} spectra cannot be related to temperature as the theory of simple QED based on the Planck law precludes the NPs of any material from having the heat capacity to increase in temperature upon absorbing heat. What this means is the notion of temperatures inferred from nanothermometers has no meaning. A brief description of simple QED is presented from which the validity of temperature measurement by nanothermometers is placed in question.

Keywords: White light, graphene, nanothermometers, Planck law, simple QED

I. INTRODUCTION

Laser induced white light (WL) from graphene [1] is limited by the lack of a band gap while thermal emission of single and multiple atom graphene layers under CW excitation is weak because the Planck law precludes [2] temperature increases. The WL spectra of graphene is are shown in Fig. 1.

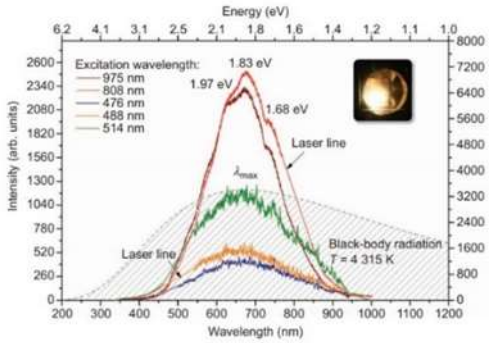

Figure 1. Graphene WL Spectra

Fig. 1 shows all WL spectra span the VIS range 400 - 900 nm for VIS laser excitation wavelengths and are centered near 660 nm. The spectra are unusual as both up and down conversions are observed: up-conversion at 808 and 975 nm and down-conversion from 476 nm. The graphene samples fabricated from layered graphene are cylindrical: diameter 6 mm, length 2 mm, and therefore nanoscale effects can be dismissed in explaining the anomalous spectra. Moreover, the spectra cannot be explained thermally as estimates of sample temperature < 900 K are far below BB effects as illustrated for 4315 K. Not shown in Fig. 1 is the WL emission from graphene ceramics clearly observed at cryogenic temperatures as low as 10 K. The WL spectra from graphene is unusual.

II. PURPOSE

The purpose of this paper is to propose the graphene WL is actually produced by the Erbium-Yttrium Oxide (Er^{+3}: Y_2O_3) NPs used as nano thermometers which are encrusted in the surface of the graphene samples. Simple QED theory of nanoscale heat transfer based on the Planck law is described and applied to explain the WL observed from graphene.

III. BACKGROUND

Simple QED heat transfer [3] at the nanoscale evolved a few decades ago from the observation that near-field theories [4-6] were based on classical heat Q flow by temperature fluctuations by Rytov and others. In contrast, simple QED based on the Planck law denies the existence of temperature fluctuations [3] in the near-field, and to nanoscale heat transfer, in general. Since heat transfer without temperature is significantly different, the Planck law was ignored, the consequence of which is an innumerable number of meaningless papers in the literature.

Simple QED follows the Planck law by conserving heat Q by non-thermal EM waves as depicted in Fig. 2.

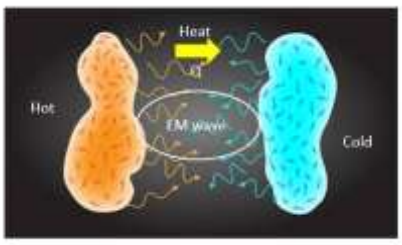

Figure 2. Simple QED heat transfer

Simple QED based on the Planck denies atoms in nanostructures the heat capacity to change in temperature. Consider the average Planck energy E of the atom mediated by the Bose distribution,

$$E = \frac{\frac{hc}{\lambda}}{\left[\exp\left(\frac{hc}{\lambda kT}\right) - 1\right]} \qquad (1)$$

and at 300 K is plotted in relation to classical physics in Fig. 3.

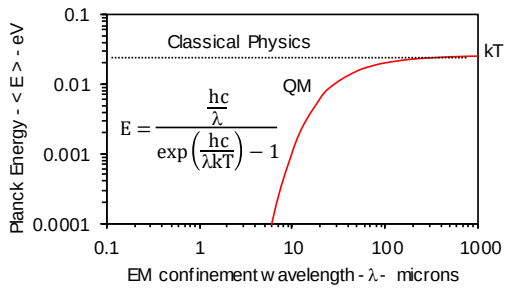

Figure. 3: Planck law of QM at 300 K
In the inset, E is Planck energy, h Planck's constant, c light speed, k Boltzmann's constant, T temperature, and λ the EM wavelength.

Fig. 3 shows the Planck law at 300 K follows classical physics allowing the atom to have kT heat capacity and change temperature for all EM wavelengths $\lambda > 200$ μm. But for $\lambda < 200$ μm, the Planck law differs as the kT heat capacity dramatically decreases, e.g., a nanoparticle (NP) having heat capacity $E = 100$ μeV at $\lambda \sim 6$ μm has heat capacity over 2 orders of magnitude lower than at $E = 0.0254$ eV where temperature changes occur upon absorbing heat. At $\lambda = 4$ μm, $E = 1$ μeV the kT heat capacity (not shown) is lowered over 4 orders of magnitude. In the near-field for $\lambda < 100$ nm, the kT heat capacity of the atom may be said to vanish.

III. THEORY

Simple QED is the consequence of the Planck law denying atoms in nanostructures the heat capacity to increase in temperature upon the absorption of heat. QED stands for quantum electrodynamics, a complex theory based on *virtual* photons advanced by Feynman [7] and others. Simple QED is far simpler only requiring the heat capacity of the atoms in nanostructures to vanish allowing conservation to proceed by the creation of *real* photons comprising EM waves that form across the nanostructure.

Similar to atomic quantum states described by electrons in discrete orbitals, simple QED quantum states are dependent on the dimension d of the nanostructure over which the EM waves form. The Planck energy E of a simple QED wave travelling across a distance d of a nanostructure is given by the time τ for light to travel across and back, $\tau = 2d/(c/n)$, where n is the index of refraction of the material. Hence, the Planck energy E of the simple QED photons is, $E \sim h/\tau$ having wavelength $\lambda = 2nd$,

$$E = \frac{hc}{2nd} \qquad (2)$$

To illustrate simple QED, consider heat flux Q having wavelength $\lambda_o >> d$ heating a nanoparticle (NP) of diameter d as illustrated in Fig. 4.

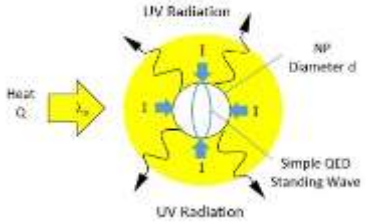

Figure 4. Heating of a NP

Importantly, heat flux Q absorbed by the NP must be placed under brief EM confinement to produce the standing simple QED waves. The EM confinement is not produced by some structuring of the NP surface, but rather produced by the heat Q flux itself.

EM confinement is the consequence of the Planck law denying NP atoms the kT heat capacity to allow the temperature changes to conserve heat Q by Fourier diffusion. Hence, the heat Q cannot penetrate the NP surface, the momentum I of which providing the EM confinement. Indeed, heat Q may only be conserved by an EM wave transiting across and back the NP diameter d in the time $\tau = 2nd/c$ giving the Planck energy E of the wave, $E = h/\tau = hc/2nd$.

The EM confinement at the NP surface is the brief inward spherical momentum I shown as blue arrows in Fig. 4. Here, U is the energy from the heat flux Q acting over an increment of time Δt, $U = QA \cdot \Delta t$, where A is the NP surface area, the units of S and Q ~ Wm^{-2} and U ~ J giving momentum $I = U/c \sim Nt \cdot s$. Over time Δt, N simple QED photons having momentum $I_P = h/2nd$ are created, where $N < I/I_P$. Once $NI_P > I$, the simple QED waves are emitted to surroundings.

Of interest, simple QED photons are created from the thermal surroundings alone. Consider a NP in the ambient environment at temperature T. The Planck law gives the heat flux Q_T as radiant thermal power energy density,

$$Q_T = \left(\frac{2c}{\lambda^4}\right)\frac{\frac{hc}{\lambda}}{\left[\exp\left(\frac{hc}{\lambda kT}\right) - 1\right]} \qquad (3)$$

The number N_T of simple QED photons created from the ambient at temperature T is $N_T = U_T V/E$, where $U_T = Q_T \cdot \Delta t$, V volume, and $E = hc/2nd$. The momentum $I_T = U_T/c$ and $I_P = N_T h/2nd$.

The importance of the Planck law in denying NP temperature fluctuations means Brownian motion ceases in the NP. In effect, the thermal heat flux Q_T produces momentum I_T because of the temperature gradient with the NP surface at absolute zero.

IV. DISCUSSION

The WL mechanism sought in producing Fig. 1 spectra was thought [1] the up-conversion of the 808-975 nm CW excitation in graphene to higher energy emission at peak intensity at 670 nm and even beyond to a lower intensity at 470 nm leading to the suggestion of cascade multiphoton processes.

However, the Fig. 1 spectra peak near 660 nm may have nothing to do with graphene, but rather in the down-conversion of 258 nm UV excitation absorbed in the Er^{+3} - Y2O3 NPs to produces the 661 nm line shown in Fig. 5.

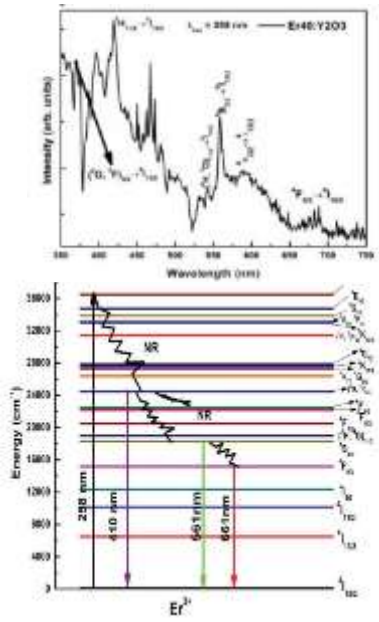

Figure 5. Down Conversion: Er^{+3} - Y2O3 at 258 nm UV

But the Fig. 1 spectra of graphene [1] was not excited by 258 nm UV, but rather over the range from 808-975 nm to 470 nm. Nevertheless, simple QED up converts the 808-975 nm excitation absorbed in the NPs to UV at 258 nm. From Eqn. 2, E = hc/2nd, $\lambda = 2nd$. The mean grain diameter d ranged between 30-150 nm. For Ytterbium based [9] glasses, the refractive index n ~ 1.75, suggests UV at 258 nm is created in NPs having $d < \lambda/2n \sim 74$ nm, but cannot be confirmed as NP sizes for given spectra are not given.

Regardless, simple QED shows that down-conversion and not up-conversion from 808-975 nm excitation occurs in NPs. Up-conversion needs multi-photon processes to convert low energy states to higher energy, a problem that has never been resolved for up-conversion in NPs prior to simple QED.

In contrast to simple QED, the up-conversion [8] of Er^{+3} - Y2O3 NPs is given in Fig. 6.

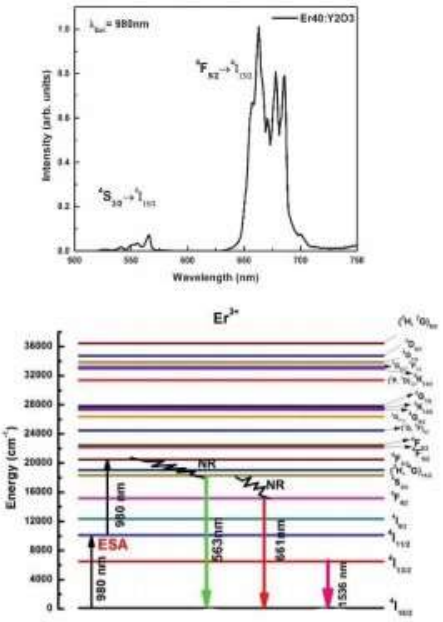

Figure 6. Up Conversion: Er^{+3} - Y2O3 at 258 nm UV

The Up-conversion process [8] is complex, but begins in Fig. 6 with the absorption of a 980 nm photon, the absorption leading to the energy transition through an intermediate state where due to absorption of a second 980-nm wavelength photon results in the transition to excited state absorption and emission at 661 nm.

In contrast, Up-conversion by simple QED is far simpler. For $\lambda = 661$ nm, the NP diameter $d < \lambda/2n \sim 190$ nm which means d ~ 150 nm in the range of available Er^{+3} - Y2O3 NPs.

The conclusion that Er^{+3} - Y2O3 NPs are the source of graphene spectra [1] is supported by spectra of materials [10] used in nano-thermometry. The Fig. 1 spectra is very similar to Er^{+3} shown in Fig. 7.

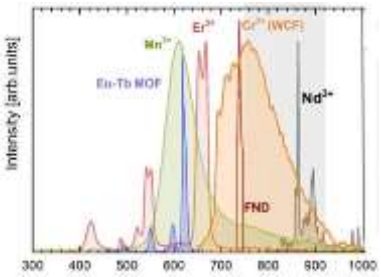

Figure 7. Erbium Er^{+3} spectra

Unlike graphene absent a band-gap, WL is expected from Erbium Er^{+3} having a mix of emission lines across the VIS color spectrum from 400-700 nm as illustrated in Fig. 8.

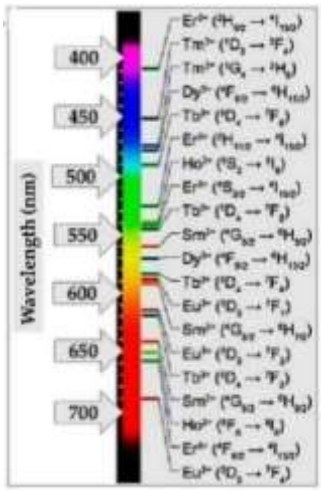

Figure 8. WL from Er^{+3} across the VIS spectrum

V. CONCLUSIONS

Graphene alone absent a band-gap cannot produce WL.

WL observed from graphene ceramics is caused by encrusted Er^{+3} - Y2O3 NPs thought to act as nanothermometers to measure graphene temperature.

The emission from NPs of Er^{+3} - Y2O3 has nothing to do with the temperature of the graphene as temperatures are precluded at the nanoscale by the Planck law.

The long thought notion that CW laser excitation is Up-converted in NPs to higher energy photons by complex multi-photon transitions is superseded by simple QED.

Depending on NP diameter and refractive index, simple QED may red or blue shift the frequency of absorbed CW laser excitation to photons having Planck energy $E = hc/\lambda$ and wavelength $\lambda = 2nd$.

.

REFERENCES

[1] Strek W., et al. [2015] Laser-induced white-light emission from graphene ceramics–opening a band gap in graphene. Light: Science & Applications doi:10.1038/lsa.2015.10.
[2] Planck M. [1900] On the Theory of the Energy Distribution Law of the Normal Spectrum. Verhandl. Dtsch. Phys. Ges., 2:2-37.
[3] Prevenslik T. [2021] White light from graphene ceramics. nanoqed.org.
[4] Mulet, J. P., et al., [2002] Enhanced radiative heat transfer at nanometric distances. Microscale Thermophysical Engineering 6:209-222.
[5] Joulain, K., et al. [2005] Surface electromagnetic waves thermally excited: Radiative heat transfer, coherence properties and Casimir forces revisited in the near field. Surface Science Reports, 57: 59-112.
[6] Shen S., et al. [2009] Surface phonon polaritons mediated energy transfer between nanoscale gaps. Nano Letters. 9:2909-2913.
[7] Feynman R., QED: The Strange Theory of Light and Matter. Princeton University Press, 1976
[8] Peddi S.P., et al. [2017] Up and Down conversion Luminescence Studies of Erbium Doped Yttrium Oxide Nanoparticle for Sensing Applications. Scientific Conference - Surface Science -Applications (CSSA-20170) College of Science-Aljouf University, May 1-2. http://vrgs.ju.edu.sa/jer.aspx
[9] Agrawal S., Dubey V. [2014] Down conversion luminescence behavior of Er and Yb doped Y2O3 phosphor. Journal of Radiation Research and Applied Sciences, 7:601-606.
[10] Bednarkiewicz A., et al. [2020] Standardizing luminescence nanothermometry for biomedical applications. Nanoscale, DOI:10.1039/D0NR03568H
[11] Marciniak L., et al. [2017] Size dependent sensitivity of Yb^{3+}, Er^{3+} up-converting luminescent nanothermometers, J. Mater. Chem. C, DOI: 10.1039/C7TC02322G.
[12] Cesaria M, Di Bartelo B. [2019] Nanophosphors-Based White Light Sources. Nanomaterials, 9:1048 https://doi.org/10.3390/nano9071048