Suggested design of gold-nanoobjects-based terahertz radiation source for biomedical research

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Abstract

Gold nanoparticles (GNPs) may serve as devices to emit electromagnetic radiation in the terahertz (THz) range, whereby the energy is delivered by radio frequency or microwave photons which will not by themselves induce transitions between sparse confinement-shaped electron levels of a GNP, but may borrow the energy from longitudinal acoustic (LA) phonons to overcome the confinement gap. Upon excitation, the Fermi electron cannot relax otherwise than via emitting a THz photon, the other relaxation channels being blocked by force of shape and size considerations. Within this general scope that has already been outlined earlier, the present work specifically discusses two-phonon processes, namely (i) a combined absorption–emission of two phonons from the top of the LA branch, and (ii) an absorption of two such phonons with nearly identical wavevectors. The case (i) may serve as a source of soft THz radiation (at \(\approx 0.54\) THz), the case (ii) the hard THz radiation at 8.7 THz. Numerical estimates are done for crystalline particles in the shape of rhombicuboctahedra, of 5–7 nm size. A technical realisation of this idea is briefly discussed, assuming the deposition of GNPs onto/within the substrate of Teflon\(^{\circledR}\), the material sustaining high temperatures and transparent in the THz range.

Keywords: terahertz imaging, microwave, phonons, Fermi electrons

(Some figures may appear in colour only in the online journal)

1. Introduction

The elaboration of simple and practical sources of terahertz (THz) radiation, in spite of a number of solutions presently available [1], remains an important task in biological and medical research. In particular, generation techniques have been suggested whose essential element are metal films [2–4]. In a recent work [5] we argued that the gold nanoparticles (GNPs) of special size and shape (nanobars or nanorings) may be used, under special conditions, for generating radiation at \(\sim 4\) THz. Later on [6], we suggested a scheme of turning an array of GNPs into a working unit of a THz to infra-red image converter, that would make possible a visualisation of pathological tissues which show contrast with the normal tissue notably in the THz range. We made use of the fact that longitudinal acoustic (LA) phonons have frequencies in the THz range, notably yielding (in bulk [7], or nanoparticles [8] of gold) the major peak in the density of modes at 3.9–4.6 THz. The phonons may be absorbed or emitted by the electron system, whose energy levels are quantified due to the nanoparticle’s small size. (In the following discussion, the energy steps between which the electron transitions may occur are of the order of THz photon energy). Moreover, the external electromagnetic field at different frequencies may intervene, to deliver energy to the system. Depending on the relation between respective frequencies and energy intervals, the following scenarios have previously attracted our attention:

(a) excitation by electromagnetic radiation at radio frequency (RF; say at 13.56 MHz, i.e., with the quanta energy by far inferior to the steps in the electron system); the excitation of a Fermi electron borrows energy from a LA phonon;
a subsequent electron’s relaxation returns the energy (with surplus) to phonons; the particle get heated. The efficiency of process is optimal for GNPs being compact/evenly shaped, with diameter ~5 nm (consistently with experimental findings of [9]; see [10] for details of our theoretical interpretation).

(b) Excitation of electron system by microwave radiation at 2.45 GHz, assisted by absorption of LA phonons, hindering however the relaxation channel into emitting a LA phonon by a specific choice of the particles’ size/shape, namely as nanobars or nanorings, of the length ~100 nm and the transversal diameter ~3 nm. As a result, a large part of the excitation energy will be deviated into a direct emission at THz frequency. The justification and technical details can be found in [5, 11].

In the present work, we pay attention that in the case (a), once the phonon ‘bath’ is hot enough, conditions may appear for two-phonon interaction with the electron system. Specifically, two processes are imaginable:

(c) an absorption of a LA phonon along with an emission of a less energetic one as a single act, the surplus energy being brought away with a soft THz photon;

(d) a simultaneous absorption of two LA phonons, consequently an excitation of electron to a much higher level than in a single-phonon absorption, with a subsequent relaxation via emission of a hard THz phonon.

Keeping in mind that the both phonons involved would typically belong to the major peak in the density of modes of gold, with abovementioned central frequency and width, the mean frequencies of the THz photons emitted in the processes (c) and (d) can be estimated as, say, ~0.54 THz, i.e., with the photon energy ~2.23 meV, for the soft and ~8.7 THz/36 meV for the hard processeses, correspondingly. Each of these frequencies is of specific interest for practical use. The soft radiation seems to be promising for good contrast in biological scanning: after [12] (a review; see in particular section 4.1.4 therein) and [13], the maximum difference in refractive index between diseased and healthy tissue lies between 0.35–0.55 THz, whereas the maximum difference in absorption occurs at 0.5 THz (see in particular figures 4 and 6 of the latter publication). The hard radiation, in its turn, would offer a better spatial resolution of the pathological/normal tissue boundaries.

The present work offers a simple theory analysis of the above cases (c) and (d), related to electron/two-phonon interactions, taking into account free-electron model for the metal nanoparticle, the confinement conditions, and the energy/momentum conservation laws. Differently from the spherical geometry of particles assumed in our earlier works, we proceeded here from GNPs having the shape of rhombicuboctahedra. Such shapes seem realistic in the production of GNPs; notably, the technology of their preparation with sizes of ~40 nm is outlined in [14, 15]. The particles of smaller sizes (~5–7 nm), argued to be needed for realisation of the mechanisms we outline, could be hopefully produced in near future by combination of selective etching and growth reactions.

2. Particle shape and confinement-imposed quantisation

Out of GNP shapes relevant for practical synthesis, we consider GNP in the shape of rhombicuboctahedron (figure 1(a)) as a realistic prototype, which comes about in the process of growing/etching towards cubic or octahedral nanocrystals [14, 15]. For the edge size A and facet width d, the ‘diameter’ (maximal wall-to-wall distance) of such particle is \( L = A + d \sqrt{2} \), and the volume \( V = A^3 + 3\sqrt{2}A^2d + 3Ad^2 + (\sqrt{2}/3)d^3 \). For order-of-magnitude estimates of the confinement conditions, we consider first the ‘ideal’ geometry \( d = A \) of the perfect small rhombicuboctahedron (which has however no special standing from the point of view of the GNP growth process), whose volume is \( V = 4(1 + 5\sqrt{2}/6)A^3 \approx 8.714 A^3 \), and then discuss the possible effect of variable aspect ratio \( d/A \).

Among the particle’s vibration modes there will be those propagating at, or under, the surface along closed trajectories; their energies will be very densely quantified, so that they will be able to absorb any surplus energy resulting from the electron relaxation, leading to the GNP’s heating. The ‘wall-to-wall’ vibration modes, on the contrary, will be relatively sparsely discretized. To be specific, we assume the ‘wall-to-wall’ distance \( L \) to encompass an integer number \( N \) of gold lattice parameters \( a_{Au} = 0.408 \text{ nm} \); \( L = N_a a_{Au} \).

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The electron states, in their turn, are discretized with the energy step \( \delta E \approx (4/3)E_F/N \), according to the Kubo’s formula [17, 18]. \( E_F \approx 5.53 \text{ eV} \) being the Fermi energy of gold (as immediately follows from the free-electron model of the corresponding electron density; otherwise see [19]), and \( N \) the number of gold atoms in a particle of volume \( V \). In general, \( N = V/V_{at} \) with \( V_{at} = \frac{a_{Au}^3}{4} \) (volume per atom in the fcc lattice), and \( N = 16N_{f}^3 (1 + 5\sqrt{2}/6)/(1 + \sqrt{2})^3 \) in the case of (perfect) small rhombicuboctahedron, so that

\[
\delta E = \frac{7 + 5\sqrt{2}}{6} \cdot \frac{E_F}{2N_{f}^3}, \quad E_F \approx 0.538 \frac{E_F}{N_{f}^3}.
\]

(1)

A deviation from the ‘ideal’ aspect ratio \( d/A \approx 1 \) affects the expression for the GNP volume; the resulting quantisation step, for the given particle size \( L \) (hence \( N_f \)) varies as shown in figure 1(b). For subsequent quantitative estimates one can reasonably assume that these poorly controllable variations of
the aspect ratio, combined with imperfections of the particle shape, relaxations/rounding up at the edges etc, would contaminate the quantisation step given by equation (1) to within some ±25%. The Fermi electrons, in the course of their interaction with phonons, may be in principle excited through an integer number of such steps; we’ll consider the lowest excitation only. In the two-phonon excitations outlined as processes (c) and (d) in section 1, possible matching conditions need to respect both the momentum and the energy conservation laws. It is important hereby that the momenta of phonons may change by uniform steps of \( \delta q \), whereas the energy conservation must take into account the nonlinearity of the genuine phonon dispersion law and the saturation of the electron energy quantisation step given by equation (1).

3 Here and in the following, the notation \( h \nu \) is used along with \( h \omega \) in order to justify/facilitate reference to experimental data in THz.

Figure 1. Rhombicuboctahedric gold nanocrystal discussed as a prototype GNP: (a) general view and indicated \( A, d \) dimensions; (b) the electron energy quantisation step \( \delta E \) throughout different aspect ratio values \( d/A \).

3. Case of phonon absorption–emission

For the lowest excitation of a Fermi electron, \( \delta E \) of equation (1) should match the energy difference for absorbed \( h \omega(q_1) \) and emitted \( h \omega(q_2) \) phonons, whereby \( q_1 \) and \( q_2 \) are discretized by force of particle size confinement. For numerical estimates, we consider the phonon momenta to be collinear, in the spirit of the above picture of the wall-to-wall longitudinal phonon resonating within the polyhedral particle. Then, the allowed values of \( \zeta \) are, for a given \( N_x \), identified by the step number \( s>0 \) of the incoming phonon, measured from the BZ border, and by the number of steps \( d \geq 1 \) between the momenta of two phonons with the reduced wavenumbers \( \zeta_1 = 1 - s/N_x; \quad \zeta_2 = 1 - (s + d)/N_x \). The matching condition

\[
\delta E = h \nu(\zeta_1) - h \nu(\zeta_2),
\]

that unifies equations (1) and (2), works like an equation on \( N_x \) for different trial values of \( s \) and \( d \). The graphic solution of this equation is given in figure 2(b). Whereas \( \delta E \) gradually decreases as function of \( N_x \), a number of intervals \( h \nu(\zeta_1) - h \nu(\zeta_2) \) that would nearly match \( \delta E \) can be found, with different choices of \( s \) and \( d \). The matches (_coincidences) which fall within ±25% of the electronic \( \delta E \) are marked in figure 2(b) by red crosses. Besides each mark, its corresponding \( d \) value (the number of quantisation steps by which the phonon wave number changes) is indicated; the \( s \) number (the placement of the absorbed phonon on the dispersion branch) is not of immediate importance and hence omitted. For the clarity of this figure, only those matches (\( \zeta_1, \zeta_2 \) are retained for which both the absorbed and the emitted phonons are among the most numerous ones, i.e. those within the half-

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width of the LA peak in the density of modes—or, differently formulated, those with frequencies within the upper 30% of the dispersion branch.

Understandably, for small $N_x$ values and hence sparse steps in the phonon dispersion, no matches can be found; from $N_x = 10$ on, more or less close matches start to appear. The solutions marked by the same relative displacement of the phonon momentum, i.e., by the same $d$ value, are placed along regular lines, indicated by thin blue descending lines in figure 2(b). Keeping in mind that this graphic solution can, at most, be considered for order-of-magnitude estimates, we indicate nevertheless that fairly good matchings according to equation (3) occur for $N_x = 10, 11, \text{ and then } 14 \text{ and from } 18 \text{ on}.$

Apart from the energy matching, one should consider the momentum conservation at the phonon scattering. An important observation is that the phonon momenta difference, $\hbar \mathbf{q}_1 - \hbar \mathbf{q}_2$, must stand almost at normal to the Fermi electron momentum. Indeed, $p_F = (12\pi^2)^{1/3}h/a_{\text{Au}} \approx 1.27 \times 10^{-19} \text{ g cm s}^{-1}$, and

$$\delta p_F \approx p_F \frac{\delta E_F}{E_F} = \frac{0.538}{2N_x^2} p_F, \quad (4)$$

so (for ‘minimalistic’ choice $N_x = 10$) $\delta p_F \approx 3.41 \times 10^{-23} \text{ g cm s}^{-1}$, whereas the step in the momentum value of phonon is

$$\delta(hq) = \frac{h}{N_x a_{\text{Au}}} \approx 1.62 \times 10^{-20} \text{ g cm s}^{-1}, \quad (5)$$

with the above estimates for the momenta values. The momentum value $p_{\text{ph}}$ of a THz photon that carries away the $\delta E$ energy is $p_{\text{ph}} = \delta E_F/c \approx 1.6 \times 10^{-25} \text{ g cm s}^{-1}$, so it can be neglected in the above balance.
Since the matching conditions in figure 2(b) can be, in principle, satisfied for a large variety of \((N_p, s, d)\) combinations, we argue in the following as for which conditions may be favourable for enhancing the efficiency of soft THz emission.

First, a mechanism is needed to create a sufficiently populated phonon bath from which the excitation energy for electrons will be borrowed. As mentioned in section 1, the GNP of sizes \(\sim 5-7\) nm (i.e., \(N_p \approx 12-17\)) have been reported to be efficiently heated by RF irradiation (see [9], also our interpretation of this effect in [10]), that seems quite promising in terms of applications. The skin effect depth in gold is 25 nm at 8.7 THz (for comparison: 100 nm at 0.54 THz) [21], therefore the GNP's of sizes under discussion will be transparent for the THz radiation generated, referred to above as 'soft' and 'hard'. One can see from figure 2(b) that there are only few good matchings in the sense of equation (3) for the above values of \(N_p\); however, one can presume that in practical conditions, a large area of GNP's deposited on a substrate will not be very selective and would emit throughout a certain range of soft THz frequencies. So, the GNP's preferential size is essentially chosen by a tendency to yield a convenient pumping mechanism through RF irradiation.

The second consideration would be to ensure that the relaxation of an excited electron proceeds through emitting a THz photon rather than, say, a soft longitudinal phonon. In fact, due to the bending down of a phonon dispersion branch towards the BZ boundary—see figure 2(a) and equation (2)—the minimal phonon energy \(\nu(\zeta = 1/N_p)\) exceeds by far the energy difference of phonons near the BZ boundary, \(\nu(\zeta = 1/2) = \nu(\zeta = 1 - d/N_p)\) up to the numbers of quantisation steps \(d = 5-6\) throughout \(N_p = 11-20\). Consequently, for small phonon momentum mismatch between the absorbed/emitted BZ-boundary phonons \((d = 1-2)\) the excitation energy \(\Delta E\) cannot be channelled into a zone-centre acoustic phonon because the latter is ‘too heavy’ to excite. In case of larger mismatch \(d\), the energy difference may eventually suffice for emitting a small-\(q\) acoustic phonon; however, in this case it would be impossible to satisfy the momentum conservation.

4. Case of two-phonon absorption

The relevance of processes with two-phonon absorption follows from an observation that the radius of the Fermi surface of gold is only slightly shorter than the distance to the BZ boundary. The free-electron model for a fcc-lattice monovalent metal with lattice parameter \(a\) yields

\[
k_F = \frac{1}{a} \sqrt{12\pi^2} = \frac{2\pi}{a} \left(\frac{3}{2\pi}\right)^{\frac{1}{2}} \approx \frac{2\pi}{a} \cdot 0.782,
\]

that is in fact a fairly good estimate in case of gold, whose Fermi radius measures, in units of \(2\pi/a\), \(\approx 0.778\) along \(\langle 211\rangle\) and \(\approx 0.737\) along \(\langle 110\rangle\) [22]. As we compare this to the phonon dispersion \(\nu(\zeta)\) in figure 2(a) we readily see that \(\zeta\) values 0.74–0.78 yield \(\nu = 4.30–4.38\) THz, that is within the ‘useful’ range of the phonon spectrum (within the major peak related to longitudinal phonons). An absorption of two such phonons would, in principle, promote an electron to a nearly opposite spot of the Fermi surface. We argue in the following that, for the particle sizes under discussion, the momentum conservation condition can be ‘absorbed’ by the uncertainty relation, thus enabling a certain tolerance in the exact matching of quantified electron/phonon momenta.

The absorption of two phonons of \(\approx 4.4\) THz frequency would mean exciting an electron far beyond the lowest quantisation level \(\Delta E\) of equation (1). In fact, setting \(\delta E \approx 36\) meV (that corresponds to \(\nu = 8.7\) THz) in equation (1) yields \(N_p \approx 4-5\), or \(L \approx 1.8\) nm, clearly too small to justify our present condensed matter-like argumentation and, moreover, unreasonably small for practical GNP applications we have in mind. For GNP's discussed above, i.e., \(N_p \approx 10-20\), the excitation energy \(\Delta E\) on the absorption of two phonons with reduced wavenumbers \(\zeta_1, \zeta_2\) would comprise an integer number \(m\) of minimal steps \(\delta E\) from equation (1):

\[
\Delta E = m \delta E = \hbar \nu(\zeta_1) + \hbar \nu(\zeta_2).
\]

From equation (1), \(N_p = 10\) would yield \(m \approx 12\) (\(m \approx 16\) for \(N_p = 11, m \approx 21\) for \(N_p = 12\), etc.). Because of the liberty in the choice of the matching \(m\) value, presumably it will not be difficult to find a pair of phonons whose energies would fit equation (8).

Similar to equation (4), i.e., replacing the energy dispersion for electrons by its linear approximation throughout the \(\Delta E\) range, and independently of \(N_p\), we get \(\Delta p_F \approx (p_F/2)(\Delta E_F/\Delta E) \approx 4.13 \cdot 10^{-22}\) g cm\(^{-1}\), i.e., still by a factor of \(\approx 40\) smaller than the quantisation step in the momentum of phonons, equation (5), and by a factor of \(\approx 300\) smaller than \(p_F\).

We turn now to more attentive consideration of the momentum conservation. We note that the momentum of an electron in the confined space of linear size \(L\) is subject to uncertainty (in the sense of standard deviation, taking \(L/2\) for that concerning the position)

\[
\Delta p \geq \frac{\hbar}{L} = \frac{1}{2\pi} \delta(hq) \approx 0.16 \cdot \delta(hq),
\]

\(\delta(hq)\) being the step in the momentum quantisation for phonons, equation (5). The uncertainty of \(\pm 0.16\) this value would certainly absorb the ‘perturbation’ due to the electron excitation \(\Delta p_F\) and otherwise serve as a measure of a nearly exact matching. For the two absorbed phonons being at the reduced ‘distances’ \(s_1\) and \(s_2\) from the BZ boundary, i.e., \(\zeta_1 = 1 - s_1/N_p\) and \(\zeta_2 = 1 - s_2/N_p\), the momentum conservation condition (for the case when the phonon momenta are parallel) would read:

\[
p_1 + p_2 = \frac{2\pi}{a\lambda_0} \hbar \left(2 - \frac{s_1 + s_2}{N_p}\right) = 2p_F + \Delta p_F \approx 2p_F.
\]
whence, by force of equation (7),
\[
\frac{s_1 + s_2}{N_i} = 2 \left[ 1 - \left( \frac{3}{2\pi} \right)^{\frac{3}{5}} \right] \approx 0.437.
\] (11)

Searching for nearly integer (within about ±0.16) solutions for \(s_1 + s_2\), one finds them more easily the larger the particle size \(N_i\), e.g., \(s_1 + s_2)/N_i = 5/11; 6/14; 7/16; 8/18;...\)

An a priori imaginable process of absorption of two phonons with opposite momenta would confront a problem of the smallness of \(\Delta \rho_F\). Indeed, the corresponding matching condition for momenta would read
\[
p_2 - p_1 = \frac{2\pi}{\alpha_{Au}} \frac{\hbar}{\rho_F} \frac{s_2 - s_1}{N_i} = \Delta \rho_F;
\]
\[
\frac{s_2 - s_1}{N_i} = \frac{\hbar}{\rho_F} a_{\alpha} p_F \frac{\Delta E_F}{E_F} = \frac{1}{2} \left( \frac{3}{2\pi} \right)^{\frac{3}{5}} \frac{\Delta E_F}{E_F} = 36 \text{ meV}
\]
\[
\approx 0.0025,
\] (12)
i.e., useless up to particle sizes \(N_i \gtrsim 400\). However, one cannot exclude a special situation \(s_1 = s_2\) when two phonons with exactly opposite momenta are absorbed and promote an electron to \(\Delta E\), whereby the necessary excess momentum \(\Delta \rho_F\) is ‘generated’ by the uncertainty of the phonon momenta.

Once the electron is excited via a two-phonon absorption, its relaxation cannot proceed via another channel than emission of a THz photon, since the phonon spectrum of gold does not contain phonons of corresponding frequency.

5. Discussion on practical realisation

In the above analysis, the reference was repeatedly made to GNPs in the shape of rhombicuboctahedra, for the simple reason that such particles, grown from rhombic dodecahedral seeds to the diameter of ∼35 nm, come about as intermediate stage in the controllable growth/etching process towards either cubic or octahedral particles of about double this size [14, 15]. In view of obvious distortion/surface relaxation/rounding at the edges it hardly makes sense to refer to a nominal dispersion relation for phonons in the polyhedral particle serving as a resonator. Still, wall-to-wall confinement conditions between the delimiting (100) planes of the rhombicuboctahedron seem to offer a clearly defined and realistic model. Further factors, e.g., confinement of phonons between opposite (110) or (111) faces of the rhombicuboctahedron, as well as irregularities of shape, would result in smearing out of the sharp quantisation conditions.

The interesting size of GNPs would be somehow smaller than the ∼35 nm cited above; notably, as was already mentioned, the most efficient heating by RF irradiation seems to occur for the particles of ∼5–7 nm size [9], or, in our counting, \(N_i \approx 12–17\). If our explanation [10] of this size selectivity is valid, the essential mechanism of GNP heating, via phonon-assisted absorption of electromagnetic quanta with energies much smaller than the electron quantisation step \(\delta E_F\), would hold irrespectively of the exact energy of the pumping field. Namely, one can envisage using the ‘pump frequency’ throughout the range from RF at 13.56 MHz (\(h\nu = 5.6 \cdot 10^{-5}\) meV) as in [9] up to the domestic microwave oven operating at 2.45 GHz (\(h\nu = 1.0 \cdot 10^{-2}\) meV), since the respective \(h\nu\) values remain by far inferior to \(\delta E\) of equation (1) which makes, e.g., 0.37 meV for \(N_i = 20\).

In what regards the prospects for practical realisation, three issues may deserve a discussion, namely (i) expected prospects for the THz emission power; (ii) the relevance of two-phonon processes in the general context of diverting the pumping energy into irradiation; (iii) the availability of GNPs of the desired size and uniformity.

Concerning (i), the radiation emission power ought to be, in general, scaled with the incident (microwave) radiation power, the (known) phonon density of states, and the hitherto unknown absorption efficiency of the incident radiation, \(\alpha\). With respect to the latter, we can refer to the work of Letfullin et al [23], who calculated \(\alpha\) for GNPs under irradiation by 600 W at 13.56 MHz to temperatures 300–350 K. We do not enter here into the discussion on the heating mechanisms; an overview of the situation up to 2014, emphasising existing controversies of interpretation, has been given by Collins et al [24]. Our explanation of the radio frequency heating of small GNPs was earlier suggested in [10]. Applying a ‘reverse phenomenological approach’ to the GNPs of the size interesting for us (5—10 nm), Letfullin et al [23] estimated \(\alpha\) to be of the order of 10−9. In our setup with deposited GNPs, this estimate (by particle) needs to be multiplied with the total particles number, of the order of 109 (assuming the volume distribution of GNPs of ∼104 mm−3 within the substrate of say 0.1 × 100 × 100 mm3). Under an (unrealistic) assumption that the entire energy pumped by incident radiation into the phonon bath will be channelled into the THz radiation, we arrive at an upper estimate of emission power of the order of some W. This is a quite rewarding expectation, in comparison with other available THz sources—see, e.g., figure 1 of [1]. The exact factor by which this upper estimate will be reduced due to real efficiency of the phonon–photon conversion within the GNP is so far difficult to estimate, even as we outlined above the arguments by force of which the other channels of the energy transfer are likely to be blocked, or suppressed.

Concerning (ii), a recent paper by Carles et al [25] dealing with phonon spectra of GNPs may offer some clue. A considerable depletion of the LA peak by as much as ∼1/3 compared to the case of bulk gold might, in our opinion, reveal two-phonon processes. This would mean that the phonons from the LA peak are, in part, spent on soft THz emission (hence the depletion), returning the rest of energy into vibration spectrum (hence the latter’s apparent shift to the left by ∼0.5 THz). Considering the observed ∼1/3 depletion as an (utterly optimistic) measure of the importance of two-phonon processes, the soft THz emission seems plausible and just needs to be searched for.

Concerning (iii), the cited work by Carles et al [25] has been done on homogeneous enough sets of GNPs, with mean diameters as small as 6.6 and 8.0 nm. Battie et al [26]...
described characterisation and (in part) preparation of GNP arrays of different shapes and sizes, whereby the set indicated as F1 was found to consist of spherical GNPs with mean diameters (6–7) ±2 nm. Omar et al [27] outlined the fabrication of monodisperse gold nanocubes with the average size controllably varying between 20 and 65 nm. Therefore the technologies of synthesis (and deposition on a convenient substrate) of GNPs covered by our previous discussion seem to be within immediate reach.

In a practical design, the GNPs need to be fixed on/in some substrate transparent for RF and THz irradiation (figure 4), well isolating the generated heat in order to channel the RF energy into phonon bath and then THz emission, rather than dissipating into the substrate. The Teflon® seem to be a convenient material for this, as has been discussed in [6], citing its transmission properties, among other THz-relevant materials, from [28]. Preparation methods for aqueous dispersions of polytetrafluoroethylene have been described by patents [29–32]; commercially produced GNPs suspended in water (colloidal gold) are also available, therefore the fabrication of Teflon®-embedded GNPs seems feasible. Their irradiation with standard sources (RF in the MHz range, or a microwave oven operating at 2.45 GHz) would generate heating up to 260° (the maximal working temperature sustainable by Teflon®) and channel the energy of thus induced phonons into THz radiation. An advantage over existing THz sources is an absence of sophisticated or expensive active elements and a potentially large cross-section of the THz beam, limited only by the size of the array of substrate-embedded nanoparticles. Focusing the beam with THz lenses [33] would, if necessary, correspondingly enhance the THz power density.

In view of further enhancing the THz radiation yield, it could be useful to increase the number of Fermi electrons within the nano-object. This can be achieved by using the metals characterised by an elevated density of electronic states at the Fermi level, e.g., Pd, Pt or Ni, or doping the GNPs with metal impurities known to place a pronounced density of states peak at $E_g$. Obviously, a simple free-electron model will not be valid for estimating the parameters of such particles.

Along with compact GNPs, gold nanobars with lengths up to micrometres and transversal size of ≈5 nm can be presumably used for generating THz radiation, via ‘conversion’ of longitudinal phonons propagating along the nanobar. The basic principles of such generation have been earlier addressed in [5]. Like in the case of compact GNPs, conditions can be created for two-phonon involvement in such generation, either via absorption–emission of phonons, accompanying an emission of ‘soft’ (difference energy) THz photon, or via two-phonon absorption resulting in ‘hard’ (summary energy) THz photon emission. The limiting cases and criteria for such processes will be discussed elsewhere.

6. Conclusion

Summarising, the possibility of THz generation by GHz-irradiated arrays of metallic nanoparticles deposited on (or, embedded into) a dielectric (suggested: Teflon®) substrate, addressed in previous works, is now extended over the inspection of a possibility to emit soft THz (at ≈0.54 THz) and hard THz (at ≈8.7 THz) radiation via two-phonon processes. We do not know how a relative outcome of such processes can be tuned; they seem simply to contribute to the total emission yield. However, soft or hard ranges of the spectrum can be selected by appropriate filtering [34]. The two ranges may have specific (distinct) advantages, e.g., for medical screening of tumours, or wound inspection under bandages. The soft 0.54 THz range enhances the contrast in representing the normal vs pathologic tissues, whereas the hard 8.7 THz range enhances the spatial resolution, both radiation ranges being harmless for living organisms.
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