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Microwave absorption by small dielectric and semi-conductor coated metal particles

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ABSTRACT

The presence of the oxide coatings on conducting metal particles is often ignored in the calculations of microwave absorption. However, we find that the optical properties of the coatings play a significant role in enhancing or suppressing the absorption of electromagnetic energy. Here, we solve the Mie scattering equations numerically to separate and quantify the role of electric and magnetic field absorption from microwaves at 2.45 GHz by small metal spheres coated with dielectric or semi-conducting materials. The range of size and conductivities of the metal particles and the optical properties of the coatings are chosen for their practical importance. We also provide simple approximate expressions for the absorption per unit volume by coated spheres in the small particle limit which agrees very well with the exact Mie solution. We have demonstrated that for highly conducting particles coated with a material of low conductivity, the electric field absorption depends *only* on the optical properties, and the volume fraction of the coating. In contrast, the magnetic field absorption depends only on the properties of the core which is the same as the bare metal. We find that the power absorbed by coated particles via the electric field is maximized when loss tangent, $tan\delta$~1. A key result of this study is that a thin layer of lossy coating (~15% of the particle size) on highly conductive particles will significantly enhance (up to a factor of 10^5) both the power absorbed from the E-field and the total power absorbed.

1. Introduction

Microwave processing of materials encompasses a broad field of commercial importance including usage in chemical processes such as catalysis [1], material sintering [2] and combustion [3] as well as in biological diagnosis [4] and drug delivery [5]. Traditional heating processes heat from external conduction where the exterior is naturally hotter than the interior. However, microwaves heat by volumetric heating, which often leads to more uniform heating [6]. This behavior has immense significance in engineering chemical reactions [7,8], as in the instance of controlling exothermic reactions [9,10]. Beyond this, selective heating is often necessary in processing of material mixtures [11].

Microwaves are electromagnetic waves with frequency ranging from 300 MHz to 300 GHz out of which 2.45 GHz is widely used commercially. Hence, throughout this text microwaves will refer to 2.45 GHz frequency. To engineer new material processing technologies based on microwave heating, an understanding of the interaction of microwaves with materials based on their electromagnetic properties is necessary. The two most important electromagnetic properties of materials are the relative complex permittivity ($\varepsilon_r = \boldsymbol{\varepsilon}'_r + i\varepsilon''_r$) and the relative complex permeability ($\mu_r = \mu'_r + i\mu''_r$). Here ε'_r and $\mu'_r$are known as the dielectric constant and magnetic permeability respectively, whereas $\varepsilon''_r$and μ''_r are known as the dielectric loss and magnetic loss respectively. Qualitatively, a higher dielectric loss tangent ($tan\delta = \varepsilon''_r/\varepsilon'_r$) and magnetic loss tangent ($tan\delta = \mu''_r/\mu'_r$), give a higher absorption of microwaves [12]. For non-magnetic particles, the relative complex permeability is considered to be 1.0 (same as free space value) as magnetic hysteresis losses are negligible. In this case, the dielectric loss, which includes losses due to both oscillation of induced dipoles by the electric field and eddy current generated by the magnetic field [13], is a key parameter in determining the amount of electromagnetic energy absorbed by the particle.

Extensive research has been conducted on the interaction of microwaves with "good" dielectric materials, as most of the early microwave-based technologies have focused more on microwave propagation than microwave absorption [15]. However, the interaction of microwaves with lossy dielectric materials and metal-

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lic conductors are extremely important to understand microwave heating of these materials. Microwave heating of metal powders have wide application in a variety of fields such as activation of combustion reaction of energetic metal powders [16] and activation of metal nanoparticle catalyzed reactions [17]. Hence, a model to study the optimized conditions for heating of conducting metal particles with a dielectric or semiconductor coating, which is often the case, is extremely desirable.

Studies focusing on the exact solutions for spherical conducting particles [18] have showed the dominance of induced magnetic dipole absorption over induced electric dipole absorption by conducting spheres as the particle size increases from nanometers to micrometers. As such, metallic (non-magnetic) powders have peak absorption when placed at the magnetic field maximum [13]. Most metals naturally form a native oxide shell and this should be accounted for in any analysis, particularly when dealing with nanoparticles where the volume fraction of the oxide may be significant. This also leads one to consider applying coatings to metallic particles to moderate or enhance the optical interactions. One approach to understanding the role of a dielectric coating is to employ an effective-sphere model which has been extensively applied in the visible region [19]. Studies of coating in the microwave region are limited [20] and thus warrant further attention.

The objective of this paper is to provide insights into the influence of the electrical properties and thickness of coatings on metal particles with various conductivities and sizes. The scope of this study is limited to using 2.45 GHz frequency due to its commercial prevalence. We employ an exact solution approach which enables one to separate and quantify the role of the electric (E-field) and magnetic field (H-field) on the effect of various coating on the absorption per volume as a function of the size and conductivity of the core particle. These examples maybe used as a baseline to explore the role of various coatings on the absorption of microwaves at 2.45 GHz by metal particles.

2. Modeling of absorption of microwaves by conducting particles

Absorption by a single spherical particle was calculated using Mie scattering theory. To standardize our calculations in terms of area irradiated and power delivered, we assume an area of 1 m^2 is uniformly irradiated with an electromagnetic power deliverance of 1 W, which gives an incident intensity (I_0) of 1 W/m^2. In this study, particles of sizes ranging from the nanometer scale to the millimeter scale are considered, which are much smaller than the wavelength at 2.45 GHz (~12 cm). Our analysis is restricted to low volume fractions (i.e. 0.01 or less) as assumed by [18] removing the need for local field corrections. Hence, the scattered radiation can be neglected [18] and single particle approximation to compute the absorption of electromagnetic radiation using Mie theory is justified.

Computations have been performed for homogeneous conductive spheres and for coated spheres with a conductive core coated with a dielectric or semi-conductive coating. Following the theory of prior works [18], the dielectric losses of the conductive core has been obtained from the respective conductivities (σ), ranging between 10°–10^8 S/m, using the Drude model, from which the real component of the dielectric constant of the conductors are assumed to be null. This gives the relation between the relative complex permittivity and the conductivity, $\varepsilon_r = i\sigma/\omega\varepsilon_0$, where ω is the angular frequency of microwaves and ε_0 is the universal permittivity of free space. The values of ε_r for the dielectric or semiconductive coatings can be expressed as $\varepsilon_r = \varepsilon'_r(1 + i\,tan\delta)$, where $tan\delta = \varepsilon''_r/\varepsilon'_r$ is the loss tangent as discussed in Section 1. We will show later in this paper that for a fixed $tan\delta$, the effect of an increase in $\varepsilon_2{}'$ is relatively small. We therefore assumed $\varepsilon'_r = 1$ and the loss tangents ($tan\delta$) are assumed to be in the range of 10^{-3}–10°, for computation of the exact solutions. The values chosen for $tan\delta$ represents the optical properties for a range of materials which includes dielectrics and semi-conductors. For example, alumina has a $tan\delta$ of 10^{-3} whereas graphite has a $tan\delta$ of 10^{-1} [14]. All the materials considered are non-magnetic and hence the relative magnetic permeability (μ_r) has been assumed to be unity for all cases.

Absorption cross-sections (C_{abs}) for the homogeneous and coated spheres were computed using the BHMIE [21] and BHCOAT subroutines [21] . The product of the absorption cross-section with the incident intensity per unit volume of particle (V_p) gives the absorbed power density (P) [21] as expressed in Eq. (1).

$$P = \frac{C_{abs} I_0}{V_p} \tag{1}$$

3. Theory

3.1. Electric and magnetic dipole absorption by bare metal conductors

The Mie scattering theory for homogeneous spheres, relates the absorption cross-section of a single particle to the wavelength (λ) and Mie coefficients, a_n and b_n by Eq. (2) [21].

$$C_{abs} = \frac{\lambda^2}{2\pi}\sum_{n=1}^{\infty}(2n+1)Re(a_n + b_n) - \frac{\lambda^2}{2\pi}\sum_{n=1}^{\infty}(2n+1)\left(|a_n|^2 + |b_n|^2\right) \tag{2}$$

Here, Mie coefficients, a_n and b_n are functions of complex permittivity ($\varepsilon_r = \varepsilon'_r + i\varepsilon''_r$) and size parameter, $x = 2\pi r/\lambda$, as expressed in Eq. (S1) in supplementary information, where r is the particle radius. The Mie coefficients have physical significance, where a_n is responsible for the E-field absorption, with a_1 being commonly known as the electric dipolar term, and b_n is responsible for the H-field absorption, with b_1 being commonly known as the magnetic dipolar term. The magnetic dipolar term accounts for the conduction losses due to the generation of eddy currents by the H-field of microwaves.

The first terms of the series for a_1 and $b_1$are calculated from Eq. (S1) and Eq. (S2) in the supplementary information. In the limit $x \ll 1$, the terms with the lowest power of x are given by:

$$a_1 = -\frac{i2x^3}{3}\left(\frac{\varepsilon_r - 1}{\varepsilon_r + 2}\right)$$
$$b_1 = -\frac{ix^5}{45}(\varepsilon_r - 1) \tag{3}$$

For nanoparticles at microwave frequencies, these expressions provide good approximations to $a_1$and b_1. From Eqs. (1-3), one obtains the following expression for the electric component of the power absorbed per volume:

$$P_E = \frac{18\pi}{\lambda}\frac{\varepsilon''_r}{(\varepsilon'_r + 2)^2 + \varepsilon''^2_r}I_0 \tag{4A}$$

One feature of this equation is that the volume specific power absorbed due to the E-field is independent of the particle radius (no x dependence). A second feature is that for $\varepsilon''_r \gg \varepsilon'_r$, which is the case for high conductivity metallic particles, the power absorbed is inversely proportional to the imaginary part of the relative permittivity and thus insensitive to ε'_r, which is close to zero for high electrical conductors (e.g. metals).

The corresponding expression for the magnetic component of the power absorbed per volume is given by:

$$P_H = \frac{\pi x^2}{5\lambda}\varepsilon''_r I_0 \tag{4B}$$

Hence according to Eq. (4A) and (4B), for highly conducting particles (large ε''_r), the dependence on x^2 results in the domination of H-field power absorption over the E-field, with increasing x. However, if ε''_r has a moderately high value then, for small values of x, P_E which is independent of x, makes the volume specific power absorbed independent of the particle size.

3.2. Electric and magnetic dipole absorption by coated metallic spheres

We now turn to the more practical problem of coated metals, most usually through their native oxide. Spherical metallic conductors have been considered with a dielectric shell around them. The complex relative permittivity and the size parameter for the conducting core is ε_1 ($\varepsilon_1 = \varepsilon'_1 + i\varepsilon''_1$) and x respectively, and that of the dielectric shell is ε_2($\varepsilon_2 = \varepsilon'_2 + i\varepsilon''_2$) and y respectively, where $x = 2\pi r_c/\lambda$ and $y = 2\pi r/\lambda$ given that r_c is the radius of the core and r is the radius of the particle. For coated spheres, the C_{abs} remains the same as Eq. (2), however the expressions for a_n and b_n are modified and expressed as a function of two additional terms A_n and B_n as shown in Eq. (S3). A_n and B_n are dependent on the properties of the core, whereas a_n and b_n are dependent on the properties of the whole particle.

The first terms of the series, A_1 and B_1, are calculated from Eq. (S3) and (S2) for which $x \ll 1$ and thus only the terms with the lowest power of x are included. The expressions obtained for A_1 and B_1 are shown in Eq. (5).

$$A_1 = \frac{2}{3}x^3\varepsilon_2^{3/2}\frac{\left(1-\frac{\varepsilon_2}{\varepsilon_1}\right)}{\left(1+\frac{2\varepsilon_2}{\varepsilon_1}\right)}$$
$$B_1 = \frac{1}{45}x^5\varepsilon_1\varepsilon_2^{3/2}\left(1-\frac{\varepsilon_2}{\varepsilon_1}\right) \quad (5)$$

Substituting Eq. (5) in the expression for a_1 and b_1 given in Eq. (S3) one obtains Eq. (6),

$$a_1 = -i\frac{2}{3}y^3\left[\frac{(\varepsilon_2-1)+\frac{x^3}{y^3}(1+2\varepsilon_2)\frac{\left(1-\frac{\varepsilon_2}{\varepsilon_1}\right)}{\left(1+\frac{2\varepsilon_2}{\varepsilon_1}\right)}}{(\varepsilon_2+2)+\frac{x^3}{y^3}(2\varepsilon_2-2)\frac{\left(1-\frac{\varepsilon_2}{\varepsilon_1}\right)}{\left(1+\frac{2\varepsilon_2}{\varepsilon_1}\right)}}\right]$$
$$b_1 = \frac{i}{45}\left[(1-\varepsilon_2)y^5-(\varepsilon_1-\varepsilon_2)x^5\right] \quad (6)$$

Considering the case where ε_1 is purely imaginary and $\varepsilon_1 \gg Im(\varepsilon_2)$. This would be the case for a highly conductive core, coated with a dielectric or semiconductor. One thus obtains Eq. (7)

$$a_1 = -i\frac{2}{3}y^3\left[\frac{(\varepsilon_2-1)+\frac{x^3}{y^3}(1+2\varepsilon_2)}{(\varepsilon_2+2)+\frac{x^3}{y^3}(2\varepsilon_2-2)}\right]$$
$$b_1 = -\frac{i}{45}x^5\varepsilon_1 \quad (7)$$

While the expression of a_1 in Eq. (7) is not valid in the limit $x = y$, it is valid provided $\varepsilon''_1(1-\frac{x^3}{y^3}) \geq 10^3$. This conditionality is obtained by comparing values of a_1 obtained from Eqs. (6) and (7) and considering the limit in which these are equal up to the 4th decimal place with respect to both real and imaginary components. In a similar manner, we have found that the expression for b_1 in Eq. (7) is valid provided $\varepsilon''_1(x/y) \geq 10^3$. Rearranging Eq. (7) to give: $a_1 = -\frac{2}{3}iy^3(\frac{\varepsilon_2-w}{\varepsilon_2+2w})$ where $w = \frac{1-x^3/y^3}{1+2x^3/y^3}$. The volume specific power absorbed from the E-field for coated particles with this approximation is given by:

$$P_E(coat) = \frac{18\pi}{\lambda}\frac{w\varepsilon''_2}{(\varepsilon'_2+2w)^2+\varepsilon''^2_2}I_0 \quad (8A)$$

From Eq. (8A), one can see that the contribution of the Electric field to the volume specific power absorbed, depends on ε_2 and x^3/y^3. This implies that the volume specific power dissipated from the E-field depends on the optical properties and volume fraction of the coating. For a fixed $\tan\delta(\varepsilon''_2/\varepsilon'_2)$ as considered in this paper, the effect of an increase in $\varepsilon_2{}'$ is relatively small. For example, if $tan\delta = 10^{-2}$ with a coating thickness of 5% of the diameter, the value of the power absorbed decreases by a factor of 7 as the value of ε'_2 is increased from 1 to 10. Therefore, the assumption of $\varepsilon'_2 = 1$ and $\varepsilon''_2 = tan\delta$ (Section 2) for computing the exact solution is justified.

The magnetic contribution to the power dissipated from the H-field is given by Eq. (8B)

$$P_H(coat) = \frac{\pi x^2}{5\lambda}\varepsilon''_1 I_0 \quad (8B)$$

Thus, the power density absorbed by the particle from the H-field is independent of the properties of the coating in this limit and only proportional to the optical properties and the surface area of the core. Notice that Eqs. (8B) and 4B are actually the same in this case. Hence, for highly conducting particles, because of the dependence on x^2 as in Eq. (8B) the H-field power absorption dominates via the core with increasing x. However, if ε''_1 has a moderately high value then, for small values of x, P_E (coat) is independent of x while P_H (coat) is a function of x^2, which results in the domination of E-field absorption by the coating. Eqs. (5)-(8) represent new expressions that can be employed to rapidly calculate optical effects for coated particles in the MW region.

4. Results and discussions

4.1. Absorption by bare metal particles

Absorbed power density from microwaves has been calculated for homogeneous spherical bare metal particles of different sizes having conductivity (σ) ranging from 10°–10^8 S/m as shown in Fig. 1(a). Similar results have been also reported by [18], but has been presented here in order to bring context to the coated cases.

In Fig. 1(a), the region where volumetric power absorption is independent of particle size corresponds to E-field dominated absorption. The H-field absorption starts dominating at the point where the power absorption increases with increasing particle size. The particle-size transition from E to H field domination, occurs at smaller particle size as the conductivity (σ) or imaginary part of the relative permittivity increases. The E-field absorption is lower for particles with higher conductivities, a consequence of the partial screening (skin depth) of the E-field within a highly conducting particle [18] as seen in Fig 1(b).

In the region of H-field dominated absorption, for smaller particles the volume specific power absorbed (Fig. 1a) is proportional to surface area (x^2) as also explained by the approximate solution in Eq. (4B) in small particle limit. The inverse dependence on particle size, for large particle sizes, is consistent with results given in [22] for $x \ll 1$ and $\sqrt{\varepsilon_r}x \gg 1$. Full expression for b_1 is required to support this. The maximum in absorption depends on conductivity and is directly proportional to the skin depth (see Table S1); $r = 2.5s$, where s is the skin depth and r is the particle radius ($x = 2\pi r/\lambda$). This matches well with the interpretations in reference [18] who found a very similar radius dependence of the maxima as 2.41 s. With further increases in particle size beyond this case, the absorption gradually decreases. The maximum value attained by the H-field power absorption is independent of σ. As shown in Fig 1(b), for particle sizes smaller than s, the eddy current generated by the H-field flows throughout the entire volume of the particles, flowing in the plane normal to the direction of the magnetic field and causing resistive energy dissipation. Eddy cur-

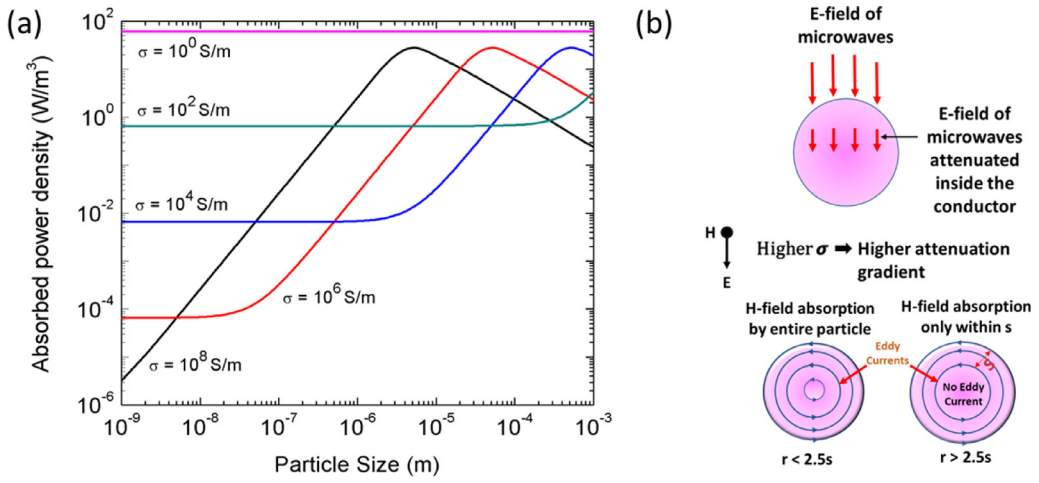

Fig. 1. Microwave power density absorbed by bare metal particles of different sizes (diameters) with different conductivities. Particles with higher conductivity have lower E-field absorption but higher H-field absorption at smaller particle sizes. (b) Schematic showing E-field screening and eddy current path in metal particles smaller and larger than the skin depth.

rent power dissipation increases with an increase in particle size until $r = 2.5s$, after which the eddy current only flows within the skin depth (s), causing the power dissipation to be restricted only within this small region, such that H-field absorption decreases.

4.2. Absorption of E-field by coated metal particles

We now turn our attention to the coated particle problem. We present the results in a manner analogous to that shown for the pure conductors (Fig. 1). Our particles are constructed whereby the coating thickness is 5% of the total particle diameter. Fig. 2(a) shows that the volume specific power absorbed from the E-field is independent of particle size and increases with $tan\delta$ of the coating ($tan\delta = \varepsilon''_2/\varepsilon'_2$) at a fixed conductivity.

Fig 2(b) shows the E-field absorbed by core-shell particles having different σ and $tan\delta$. The maximum power absorbed peaks at $\sigma = 0.5$ S/m which is $\sim 3\omega\varepsilon_0$, independent of $tan\delta$. The maxima in absorption in the case of bare metal particles is ~0.4 S/m as reported by [18] and implies that the presence of a coating does not affect the maxima of the absorption.

For conductivities in excess of 0.5 S/m, the E-field absorption gradually decreases and achieves a constant value, independent of conductivity of the core. This is the asymptotic region where the coating dominates and the core has no effect on absorption. Eqs. (7 & 8) are only dependent on the properties of the coating and hence these are applicable in this region.

Fig. 2(c) shows the dependence of E-field absorbed on $tan\delta$ for coatings with σ ranging between 10°–10^8 S/m. The absorption by the particles with different σ, peaks at the same $tan\delta$ of 1. When Eq. (8A) is expressed in terms of $tan\delta$ by replacing $\varepsilon''_2/\varepsilon'_1$ with $tan\delta$ and assuming $\varepsilon'_1/\varepsilon'_1$, the following equation is obtained:

$$P_E(coat) = \frac{18\pi}{\lambda} \frac{w\ tan\delta}{(1+2w)^2 + tan\delta^2} I_0 \tag{9}$$

From Eq. (9), the peak absorption occurs when $tan\delta = 1 + 2w$ and since $0 < w < 1$, it can be said that the maxima is $tan\delta \sim 1$. The coating absorbs power from the E-field due to the oscillation of induced electric dipoles. The power absorbed by the coating increases with the increase in $tan\delta$ of the coating, and reaches a maximum at $tan\delta = 1$. This is because the increase in $tan\delta$ implies an increase in the polarizability of the medium resulting in higher power dissipation. However, with $tan\delta > 1$, the coating material itself behaves as a conductor, and this behaves as the case described in Section 4.1, and the screening of the electric field within the coating results in the decrease in power absorption with increasing $tan\delta$. Fig. 2(d) illustrates microwave absorption within the coating by induced dipoles and the depletion layer at the interface of the dielectric or semi-conductive coating and the conductive core, driven by the chemical potential difference between the two materials. The presence of this depletion layer is well-known and previously analyzed in various studies [23–25]. The absorption due to the oscillation of this depletion layer has not been accounted in our calculations. Hence, our model may slightly underestimate the magnitude of power absorbed.

4.3. Significance of H-field absorption in coated metal particles

Absorption of the H-field and net effect of microwaves has been calculated for conductive metal particles of different sizes with conductivity (σ) ranging from 10°–10^8 S/m, coated with dielectric and semi-conductive materials having loss tangents ($tan\delta$) ranging between 10^{-3}–10° S. The coating thickness has been assumed to be 5% of the diameter of the particle, as with the previous case. Fig. 3(a) shows the H-field absorbed by metal particles of different sizes and σ, with a coating of $tan\delta = 10^{-3}$, and we find similar results to that reported previously [18] and consistent with Eq. (8B)

This is because the eddy currents can only be generated in the conductive metallic core. We have seen that the H-field absorption is independent of the $tan\delta$ of the coating and have thereby chosen only one case with $tan\delta = 10^{-3}$for representation. The maximum H-field absorption is still observed at $r = 2.5s$. The particles with higher σ, peak at lower particle sizes, similar to the case observed for bare metal particles.

4.4. Total power absorbed by coated metal particles

The total field absorbed from the microwaves have been computed for metal particles having σ of 10^8 S/m [Fig. 4] with coatings of $tan\delta$ of 10^{-3} to 10°. This is done to assess the relative importance of H vs. E fields as a function of particle size. Smaller particle sizes (nanometer range), show an increase in volume specific power absorption with increase in $tan\delta$ and is independent of particle size due to E-field domination of absorption by the coating. At higher particle sizes (micrometer range), however, the power absorbed increases for different $tan\delta$ and converges at a maximum at $r = 2.5s$; i.e. the same as that for bare metals. For particle sizes beyond the maxima, absorption decreases. These trends show that at larger sizes H-field absorption by the core is the dominant factor.

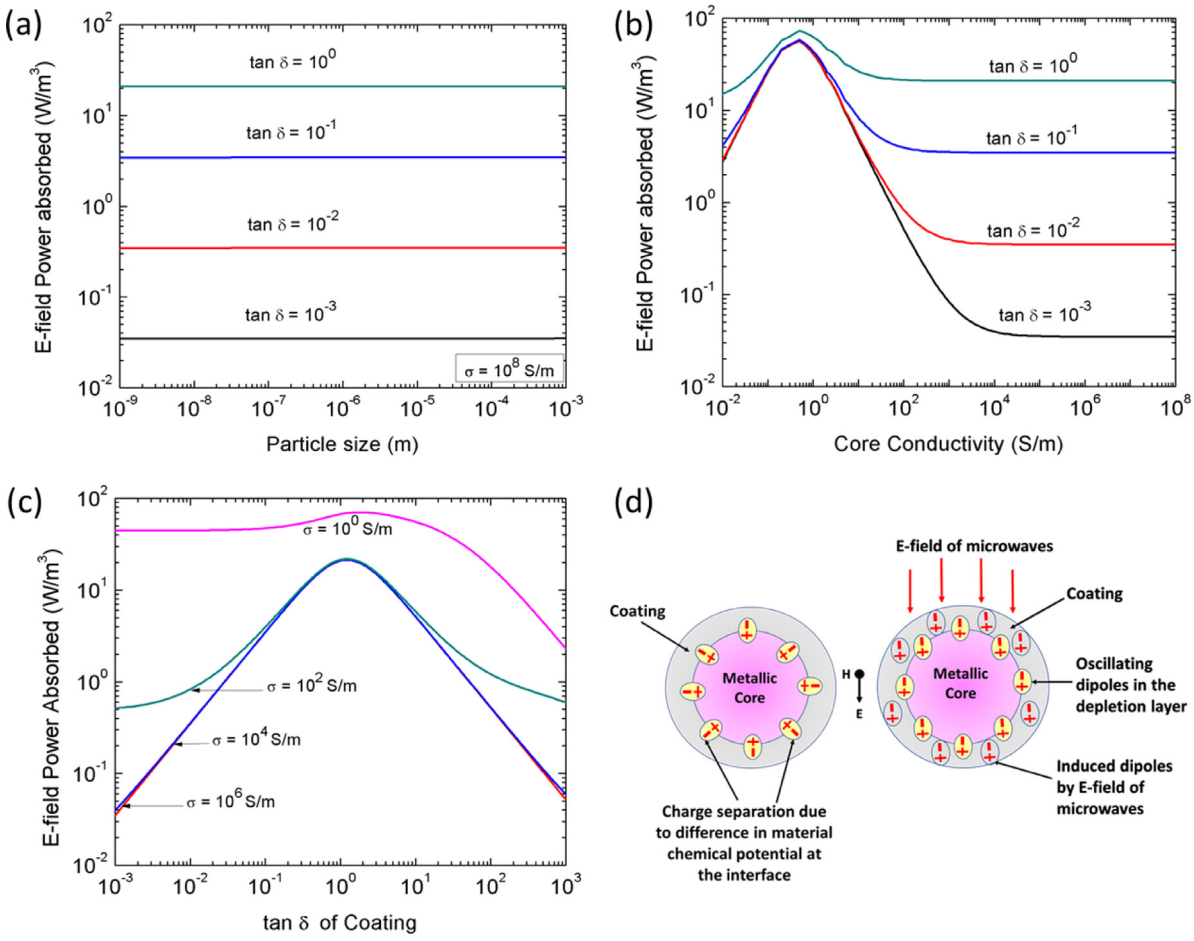

Fig. 2. (a) E-field absorbed by conducting particles (σ=10^8 S/m) having coatings with different *tanδ* (coating), E-field absorbed by conducting particles as a function of different core conductivities (b), having coatings with different *tanδ*(c). (d) Schematic showing the role of inherent (interface) and induced (coating) dipoles in absorption of E-field of microwaves by coated metal particles.

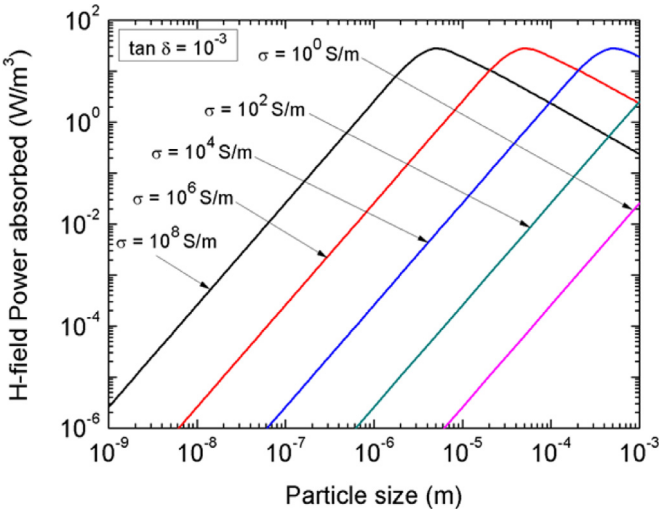

Fig. 3. H-field absorbed by conducting particles of different sizes (diameters) and conductivities (σ) having a coating of tanδ = 10^{-3}. The H-field absorption by the coated particles is the same as that of the core.

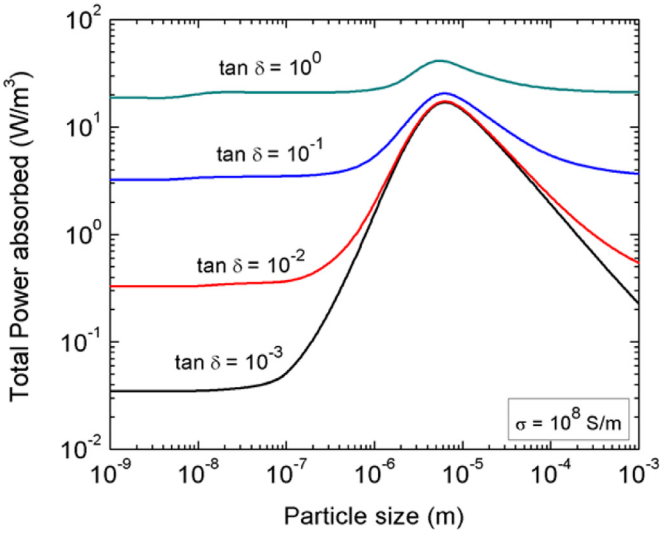

Fig. 4. Total power absorbed by conducting particles of different sizes (diameters) with σ = 10^8 S/m, having coatings of *tanδ* ranging between 10^{-3}–10^{0}.

4.5. Dependence of absorption on the thickness of the coating

To assess the role of the coating thickness, we consider two different particle sizes, in the nano (10^{-8} m) and micro (10^{-6} m) range, and with two different coatings, $tan\delta = 10^{-3}$ (dielectric) and $tan\delta = 10^{-1}$(semi-conductive). Fig. 5(a) and (b) shows a very rapid increase in absorption for very small coating thicknesses regardless of particle size, with a dielectric coating ($tan\delta = 10^{-3}$). Increases as much as two orders of magnitude are observed for an increase in coating thickness of <15%. We have already shown that E-field absorption dominates for both bare and coated metal nanoparti-

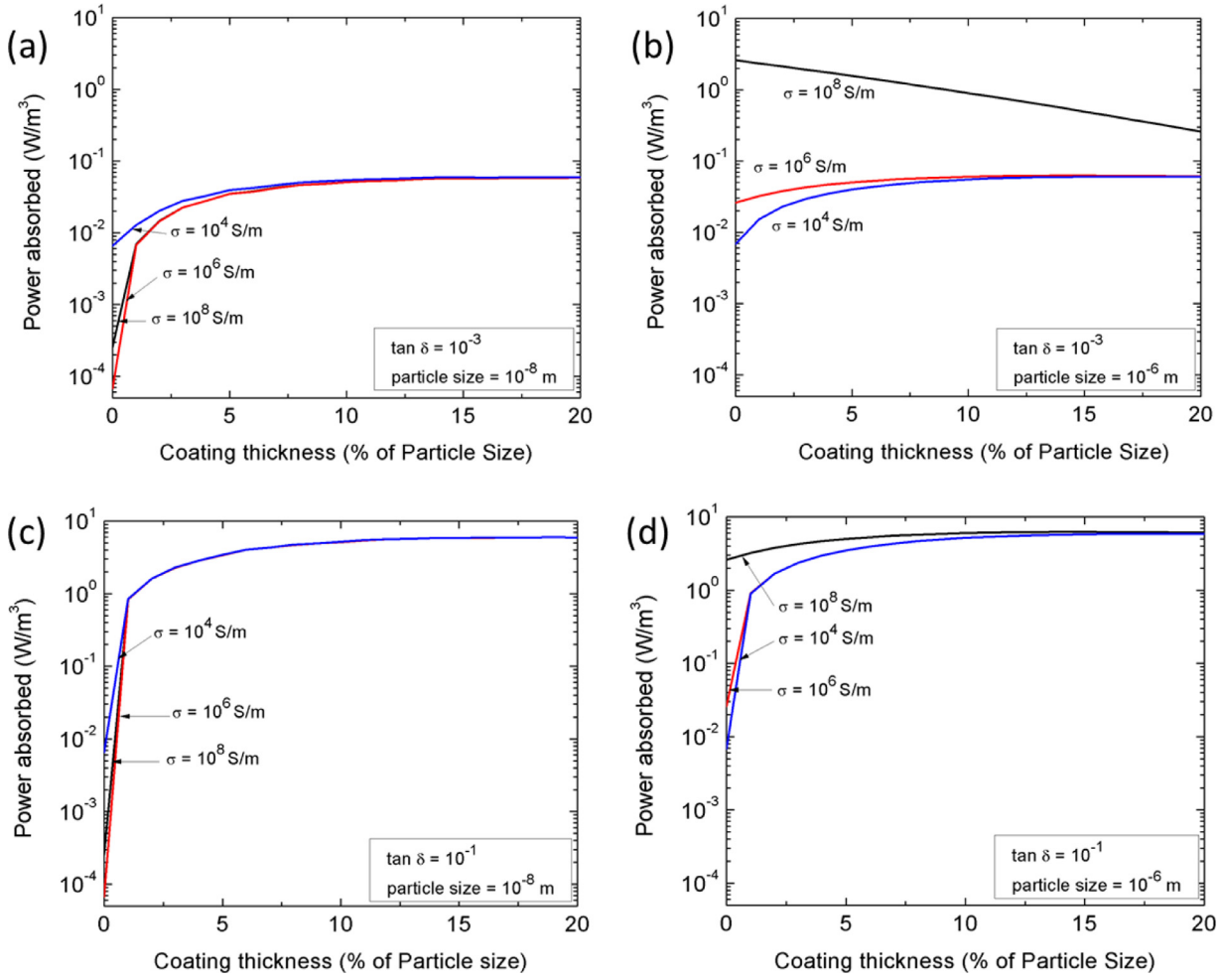

Fig. 5. Power absorbed by conductive particles having different σ, with size (diameter) of 10^{-8} m and coating of $tan\delta = 10^{-3}$ (a), with size of 10^{-6} m and coating of $tan\delta = 10^{-3}$ (b), with size of 10^{-8} m and coating of $tan\delta = 10^{-1}$ (c) and with size of 10^{-6} m and coating of $tan\delta = 10^{-1}$ (d), with different coating thicknesses.

cles (10^{-8} m). According to Fig. 5(a), at a particle size of 10^{-8} m, the E-field absorption by the coating dominates that of the core, and hence the power absorption increases with increase in coating thickness until the coating thickness is ~15% of the particle diameter. For the micron particle, as in Fig. 5(b), at high conductivities ($\sigma = 10^8$ S/m) the bare particle actually absorbs more than the coated due to the dominance of the H-field absorption. Only at lower conductivities does the coating enhance absorption due to the increasing importance of E-field absorption.

In a similar manner, Fig. 5(c) and (d) shows the case for a semiconducting coating ($tan\delta = 10^{-1}$). For the nanoparticle (Fig. 5(c)), the E-field absorbed by the coating is significantly higher than the core. Hence in these cases the absorption increases drastically with increase in the coating thickness until the coating thickness is ~15% of the particle size. At this coating thickness the absorption is significantly higher than the bare metal case as well as the case when the particles are coated with an inferior absorber of $tan\delta = 10^{-3}$. For the micron particle shown in Fig. 5(d), absorption of H-field dominates when bare, but with increase in volume of the coating, the E-field absorption by the coating becomes more important. .

In general the results show that nanoparticle absorption is very sensitive to coating thickness and achieves a maximum at coatings of ~ 15%. Microparticles, in contrast do not show quite the sensitivity to coatings, particularly if the coating is not a strong absorber or when the core is highly conductive

Because of the potential interest in this finding, we also have plotted the ratio of the power absorbed by coated particles to power absorbed by bare particles for particles of various sizes and core conductivities (σ) to show the power enhancement in coated particles compared to the bare particles. Fig. 6 represents this ratio (P_{coated}/P_{bare}) for particles of different sizes and conductivities, having a coating of $tan\delta = 10^{-1}$, with a thickness of 15% of the particle size.

For $\sigma = 10^2$–10^8 S/m, the ratio is very high for the smaller particles but decreases with increase in particle size because of the domination of the H-field absorption by the metallic core. The particles with $\sigma = 10^{\circ}$ S/m are unaffected by the coating. Hence, the coating can increase the power absorption in the case of small and conducting particles but is not so effective for large particles. All of these results have been summarized in Table 1.

To establish the validity of our approximate solutions, we have compared the results for power absorbed from the E-field (P_E) i.e. Eq. (8A) and power absorbed from H-field (P_M) i.e. Eq. (8B) to the exact Mie solutions in Fig. 7 for the case of a microparticle with a coating of $tan\delta = 10^{-1}$ and a core with $\sigma = 10^6$ S/m. The value of P_E increases by more than 4 orders of magnitude as one goes from the bare metal (0% coating thickness) to all coating (100% coating thickness). For thickness greater than 10^{-3}%, the volume specific power absorbed is a linear function of the coating thickness. However, for a coating thickness above ~10%, both the approximate and exact solutions flatten out so the absorption is nearly constant as

Table 1
Summary of absorption tendency and model equations for different domains of particle size and conductivity.

Particle size (m)	$\sigma = 10^{\circ}$–10^{2} S/m	$\sigma = 10^{4}$–10^{6} S/m	$\sigma = 10^{8}$ S/m
10^{-9}–10^{-7} (nano)	Core (H-field) dominates Eq. (8B)	Coating (E-field) dominates* Eq. (8A)	Coating (E-field) dominates Eq. (8A)
10^{-6}–10^{-4} (micro)	Core (H-field) dominates Eq. (8B)	High loss Coatings (E-field) dominates Eq. (8A)	Core (H-field) dominates Eq. (8B)

* *Domain of primary interest.*

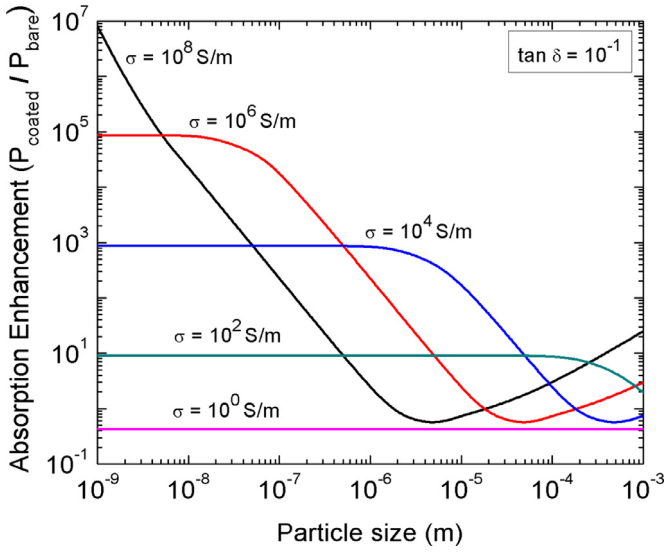

Fig. 6. The absorption enhancement in coated particles compared to the bare particles of various sizes (diameters) and conductivities.

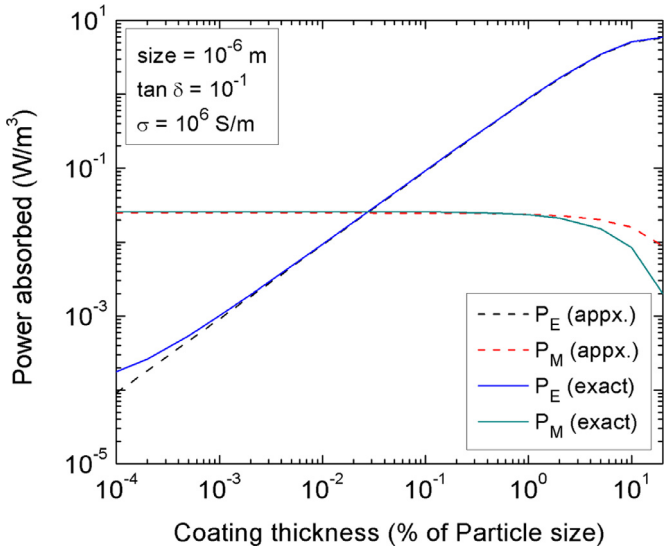

Fig. 7. Comparison between approximate and exact Mie solutions of power absorbed from the E-field (P_E) and H-field (P_M) for a particle size (diameter) = 10^{-6} m with coating $tan\delta = 10^{-1}$ and core $\sigma = 10^{6}$ S/m.

one approaches the case of 100% coating. The region where there is a discrepancy between the approximation and the exact result up to a factor of 2 is for very small coating thicknesses below ~10^{-4}%. The thickness of such a coating would be on the order of 1% of the diameter of a hydrogen atom.

The approximate solution for P_M agrees with the exact solution so long as the coating thickness is less than 1.5% of the particle size. However this latter consideration turns out to be unimportant since for coatings greater than 1.5% of the particle size, $P_E >> P_M$ in any case, and hence the breakdown of the approximate has no practical effect in estimating the total power absorbed. Thus our approximate solutions are very robust as well as simple.

5. Conclusions

In this work, we have obtained working formulas (Eqs. (5)-(8)) validated on full Mie theory calculation for microwave absorption by conducting particles coated with a semi-conductive or dielectric coating in the small particle limit, for the condition $[\varepsilon''_1 \gg \varepsilon''_2]$. The range in coating thickness and optical properties for which the formulas is valid was determined by comparing with the results using full Mie theory solutions for coated spheres. From these formulas we conclude that the E-field contribution to absorption depends only on the optical properties, and the volume fraction of the coating. In fact, from the full solution we can also infer that for coating thicknesses greater than about 15% of the particle size, absorption is equivalent to a sphere of the same size and with the same optical properties as the coating. The power absorbed from the H-field, depends only on the core properties, and is equivalent to that of the case of bare metals. The approximate solutions for E-field contribution to power absorbed agrees with the exact Mie solutions as long as the coating thickness is greater than 0.002% of the particle size, whereas that for the H-field breaks down when coating thickness is greater than 1.5% of the particle size, but is unimportant for a thicker coating in any case.

The full solution is also being presented to show the cases where the condition $[\varepsilon''_1 \gg \varepsilon''_2]$ is not satisfied. The peak value of P_E by the coated metal particles have been found when core conductivity, $\sigma \sim 3\omega\varepsilon_0$ and coating $tan\delta \sim 1$. We have shown that the presence of a thin layer (~15% of particle size) of absorbing coating can drastically enhance the absorption of nanoparticles by a factor of ~10^5 compared to bare metal particles. The effect of the coating is more pronounced for the nanoparticles, whereas microparticles are not so sensitive to the coating particularly when the coating is an inferior absorber or when the core is highly conductive. The large enhancement in case of the nanoparticles, suggests that materials scientists working with nanoparticles focus more on E-field absorbing coatings rather than focusing on the H-field absorption.

Finally we note that existing effective medium theories [19] that use volume average optical properties to solve for non-homogeneous materials such as coated spheres, are mostly based on the electrostatic approximation employing an effective complex permittivity (ε_r), while ignoring the permeability (μ_r). While this approximation may be adequate for nanoparticles, this work demonstrates that to adequately describe the absorption of microparticles; i.e. accounting for H-field absorption thorough the effective complex permeability would require development of new effective medium theories.

Author statement

Prithwish Biswas – Co- Derived the theory and did most of the calculations, wrote paper

George W. Mulholland, Co-Derived theory and was deeply involved in problem formulation and results evaluation, edited paper

Miles C. Rehwoldt, Results evaluation

Dylan J. Kline, Conducted some of the calcutions and results evaluation,

Michael R. Zachariah, conceptualized the project, directed the research and evaluated results. Wrote and edited paper.

Declaration of Competing Interest

The authors have no interests to declare.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jqsrt.2020.106938.

References

[1] Haneishi N, Tsubaki S, Abe E, Maitani MM, ichi Suzuki E, Fujii S, et al. Enhancement of fixed-bed flow reactions under microwave irradiation by local heating at the vicinal contact points of catalyst particles. Sci Rep 2019;9:1–12. doi:10.1038/s41598-018-35988-y.

[2] Mishra P, Sethi G, Upadhyaya A. Modeling of microwave heating of particulate metals. Metall Mater Trans B Process Metall Mater Process Sci 2006;37:839–45. doi:10.1007/s11663-006-0066-z.

[3] Stockman ES, Zaidi SH, Miles RB, Carter CD, Ryan MD. Measurements of combustion properties in a microwave enhanced flame. Combust Flame 2009;156:1453–61. doi:10.1016/j.combustflame.2009.02.006.

[4] Wang L. Microwave sensors for breast cancer detection. Sensors (Switzerland) 2018;18:1–17. doi:10.3390/s18020655.

[5] Larrañeta E, Lutton REM, Brady AJ, Vicente-Pérez EM, Woolfson AD, Thakur RRS, et al. Microwave-assisted preparation of hydrogel-forming microneedle arrays for transdermal drug delivery applications. Macromol Mater Eng 2015;300:586–95. doi:10.1002/mame.201500016.

[6] Dolande J, Datta A. Temperature profiles in microwave heating of solids: a systematic study. J Microw Power Electromagn Energy 1993;28:58–67. doi:10.1080/08327823.1993.11688206.

[7] Gerbec JA, Magana D, Washington A, Strouse GF. Microwave-enhanced reaction rates for nanoparticle synthesis. J Am Chem Soc 2005;127:15791–800. doi:10.1021/ja052463g.

[8] Dudley GB, Richert R, Stiegman AE. On the existence of and mechanism for microwave-specific reaction rate enhancement. Chem Sci 2015;6:2144–52. doi:10.1039/c4sc03372h.

[9] Barkley SJ, Kindem DK, Zhu K, Michael JB, Sippel T. Dynamic control of composite solid propellant flame spread through microwave eddy current heating of propellant-embedded antennas. AIAA Scitech 2019 Forum 2019. doi:10.2514/6.2019-1239.

[10] Mirzaei A, Neri G. Microwave-assisted synthesis of metal oxide nanostructures for gas sensing application: a review. Sensors Actuators, B Chem 2016. doi:10.1016/j.snb.2016.06.114.

[11] Kitchen HJ, Vallance SR, Kennedy JL, Tapia-Ruiz N, Carassiti L, Harrison A, et al. Modern microwave methods in solid-state inorganic materials chemistry: from fundamentals to manufacturing. Chem Rev 2014;114:1170–206. doi:10.1021/cr4002353.

[12] Gong C, Zhang J, Yan C, Cheng X, Zhang J, Yu L, et al. Synthesis and microwave electromagnetic properties of nanosized titanium nitride. J Mater Chem 2012;22:3370–6. doi:10.1039/c1jm13509k.

[13] Ignatenko M, Tanaka M, Sato M. Absorption of microwave energy by a spherical nonmagnetic metal particle. Jpn J Appl Phys 2009:48. doi:10.1143/JJAP.48.067001.

[14] Horikoshi S., Schiffmann R.F., Fukushima J., Serpone N. Microwave chemical and materials processing: a tutorial. 2017. doi:10.1007/978-981-10-6466-1.

[15] Dragoman M, Cismaru A, Aldrigo M, Radoi A, Dinescu A, Dragoman D. MoS2thin films as electrically tunable materials for microwave applications. Appl Phys Lett 2015:107. doi:10.1063/1.4938145.

[16] Meir Y, Jerby E. Thermite powder ignition by localized microwaves. Combust Flame 2012;159:2474–9. doi:10.1016/j.combustflame.2012.02.015.

[17] Gracia J, Escuin M, Mallada R, Navascues N, Santamaria J. Nano-heaters: new insights on the outstanding deposition of dielectric energy on perovskite nanoparticles. Nano Energy 2016;20 20–8. doi:10.1016/j.nanoen.2015.11.040.

[18] Porch A, Slocombe D, Edwards PP. Microwave absorption in powders of small conducting particles for heating applications. Phys Chem Chem Phys 2013;15:2757–63. doi:10.1039/c2cp43310a.

[19] Chettiar UK, Engheta N. Internal homogenization: effective permittivity of a coated sphere. Opt Express 2012;20:22976. doi:10.1364/oe.20.022976.

[20] Rybakov KI, Semenov VE, Egorov S V, Eremeev AG, Plotnikov IV, Bykov YV. Microwave heating of conductive powder materials. J Appl Phys 2006;99:023506. doi:10.1063/1.2159078.

[21] Bohren C.F., Huffman D. Absorption and scattering of light by small particles. New York: Wiley. n.d. doi:10.1002/9783527618156.

[22] van de Hulst HC. Light scattering by small particles. New York: John Wiley and Sons; 1958. doi:10.1002/qj.49708436025.

[23] Henz BJ, Hawa T, Zachariah MR. On the role of built-in electric fields on the ignition of oxide coated nanoaluminum: ion mobility versus fickian diffusion. J Appl Phys 2010:107. doi:10.1063/1.3247579.

[24] Monch W. On the physics of metal-semiconductor interfaces. Reports Prog Phys 1990. doi:10.1088/0034-4885/53/3/001.

[25] Di Bartolomeo A. Graphene Schottky diodes: an experimental review of the rectifying graphene/semiconductor heterojunction. Phys Rep 2016. doi:10.1016/j.physrep.2015.10.003.