Quantifying the Efficiency of Plasmonic Materials for Near-Field Enhancement and Photothermal Conversion

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ABSTRACT: Following recent advances in nanoplasmonics related to high-temperature applications, hot-electron processes, nanochemistry, sensing, and active plasmonics, new materials have been introduced, reducing the supremacy of gold and silver in plasmonics. The variety of possible materials in nanoplasmonics is now so wide that selecting the best material for a specific application at a specific wavelength may become a difficult task. In this context, we introduce in this Article two dimensionless parameters acting as figures of merit to simply compare the plasmonic capabilities of different materials. These numbers, which we named Faraday and Joule numbers, aim at quantifying the ability of a nanoparticle to respectively enhance the optical near field and produce heat. The benefit of these



numbers compared to previously defined figures of merit is that (i) they possess simple close-form expressions and can be simply calculated without numerical simulations, (ii) they give quantitative estimations in the nonretarded regime, and (iii) they take into account the nature of the surrounding medium. Within this Article, we address a wide variety of materials, namely, gold, silver, aluminum, copper, cobalt, chromium, iron, molybdenum, manganese, nickel, palladium, platinum, rhodium, tantalum, titanium, titanium nitride, tungsten, and zirconium nitride.

INTRODUCTION

Metal nanoparticles under localized plasmon resonance can be the source of optical near-field enhancement on the nanoscale, along with a pronounced heat generation. The efficiency of light and heat generation of metal nanoparticles depends on their nature, morphology, environment, and illumination wavelength.^{1,2}

So far, gold and silver have been the materials of choice for most applications in nanoplasmonics. Silver is known for its intense plasmonic response, albeit damped by sulfidation.³ Gold is known for its chemical inertia, easy functionalization, low toxicity, and localized plasmon resonances in the visibleinfrared range, making it the ideal candidate for biomedical applications.⁴ Very recently, new metals have been proposed as suitable plasmonic materials^{5–8} to tackle emerging applications of plasmonics, for example, high-temperature applications,⁹ nanochemistry,¹⁰ sensing,¹¹ or active plasmonics,¹² where gold and silver do not possess all the required properties, such as high-temperature sustainability, or catalytic activity. For these reasons, gold and silver are currently reducing their predominance in plasmonics, to the benefit of other metals, metal oxides, metal nitrides, and alloys that constitute a new emerging branch of research. Following this burgeoning variety of plasmonic materials, it becomes useful to conduct a comprehensive and comparative study in order to clearly establish the relative efficiencies of these new plasmonic materials.

In an attempt to define a figure of merit to estimate the relative efficiency of different materials in plasmonics, it was proposed to simply consider the ratio between the real part and the imaginary part of the permittivity of the material at the considered wavelength: ${}^{6,13,14} - \varepsilon'(\lambda)/\varepsilon''(\lambda)$. Even though such a figure of merit has been widely used, its applicability remains limited. First, it does not enable quantitative comparison between different materials, or between different wavelengths, and it does not involve the nature of the surrounding medium. Second, it does not seem consistent to estimate the efficiency of a plasmonic material using a single number, as plasmonic nanoparticles can have different functionalities (e.g., heat generation or optical near-field enhancement). Indeed, the search for simple close-form expressions rendering the plasmonic efficiency was mainly oriented toward near-field applications such as SERS (surface-enhanced Raman scattering), but nothing has been done in this spirit to address the heat generation efficiency, the other important function of plasmonic nanoparticles.

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In this theoretical Article, we first introduce two dimensionless parameters, which we termed Faraday and Joule numbers, aiming at quantifying the ability of a material to respectively yield efficient near-field enhancement and photothermal generation in nanoplasmonics. We give different expressions of these numbers and explain how they can quantitatively compare the efficiency of nanoparticles of different natures, in the nonretarded regime. In a second part, we detail how the definition of the Faraday and Joule numbers can be extended to describe nonspherical particles. In order to illustrate the benefits of the Faraday and Joule numbers compared to previously defined figures of merit, two practical cases are detailed where the plasmonic properties of selected materials derived from the Faraday and Joule numbers are compared with numerical simulations.

RESULTS AND DISCUSSION

Theory of Field Enhancement. As usual in physics, the case of a sphere is simple and very instructive (see Figure 1).



Figure 1. Spatial description of the system under study: a spherical metal nanoparticle of permittivity ε in a surrounding dielectric medium of permittivity $\varepsilon_s = n_s^2$ and submitted to an external electric field \mathbf{E}_0 directed along the *x* axis.

Let us consider a sphere of permittivity ε and radius *a*, standing in a uniform surrounding medium of refractive index n_s and illuminated by a monochromatic light characterized by the electric field

$$\mathbf{E}_{0}(\mathbf{r}, t) = \mathcal{R}(\mathbf{E}_{0}(\mathbf{r}) e^{-i\omega t})$$
(1)

where ω is the angular frequency of the light and $\lambda = 2\pi c/\omega$ is the wavelength in vacuum. For a plane wave illumination, one has

$$\mathbf{E}_{0}(\mathbf{r}) = \hat{\mathbf{u}}E_{0} e^{i\mathbf{k}\cdot\mathbf{r}}$$
(2)

where the norm of the wave vector **k** reads $k = 2\pi n_s/\lambda$.

In the presence of the nanoparticle, the electric field at any location $r\ \text{reads}^{15}$

$$\mathbf{E}(\mathbf{r}, t) = \mathcal{R}(\mathbf{E}(\mathbf{r}) e^{-i\omega t})$$
(3)

For a nanoparticle small enough to feature a dipolar response, simple close-form expressions can be derived. In particular, the polarizability of a sphere endowed with an electric permittivity $\varepsilon(\omega)$ reads:¹⁵

$$\alpha = 4\pi a^3 \varepsilon_s \xi \tag{4}$$

where

$$\xi = \frac{\varepsilon(\omega) - \varepsilon_{\rm s}}{\varepsilon(\omega) + 2\varepsilon_{\rm s}} \tag{5}$$

Note that in the static case ($\omega = 0$), $\xi = 1$. The enhancement factor ξ plays an important role in the underlying physics of nanoplasmonics. For instance, ξ can be used to simply express the amplitude of the electric potential outside the sphere:

$$\varphi_{\text{ext}}(r,\,\theta) = E_0 \left(r - \xi \frac{a^3}{r^2}\right) \cos\theta \tag{6}$$

The first term in brackets is the contribution of the incoming electric field, and the second term scaling as $1/r^2$ is the field created by the sphere, which is weighted by this factor ξ . The electric field can be easily calculated from eq 6, which yields a maximum electric field enhancement by a factor of $1 + 2\xi$ on the diametrically opposed apexes of the sphere at $(r, \theta) = (a, 0)$ and (a, π) :

$$E_{\max} = (1 + 2\xi)E_0$$
(7)

Note that when a nanoparticle is immersed in a static electric field ($\omega = 0$), as $\xi = 1$, the electric field is supposed to be already enhanced by a factor of 3, and the electric field intensity by a factor of 9. Substantial near-field enhancement is thus a distinctive feature of metal particles, and does not necessitate the occurrence of a plasmonic resonance. As explained later, plasmonic materials that can hardly do better than a factor of 9 in terms of near-field intensity enhancement cannot be considered as good plasmonic materials for near-field applications.

Besides E_{max} another valuable quantity is the electric field observed inside the nanoparticle. While it is canceled out due to charge accumulation in the static case, there is here a nonzero electric field inside the nanoparticle, especially under plasmonic resonance. For a dipolar sphere, the electric potential inside the sphere reads¹⁵

$$\varphi_{\rm in}(r,\,\theta) = -\frac{3\varepsilon_{\rm s}}{\varepsilon(\omega) + 2\varepsilon_{\rm s}} E_0 r\,\cos\theta \tag{8}$$

$$=(\xi - 1)E_0 r \cos\theta \tag{9}$$

The inner electric field is thus uniform and its complex amplitude equals

$$E_{\rm in} = -(\xi - 1)E_0 \tag{10}$$

In the previous paragraphs, we chose to focus on $E_{\rm max}$ and $E_{\rm in}$ for the following reasons. First, $E_{\rm max}$ expresses the ability of the nanoparticle to increase the electric field at its vicinity, the dominant parameter for applications such as surface-enhanced fluorescence, surface-enhanced Raman spectroscopy (SERS) or (bio)molecule sensing. Second, $E_{\rm in}$ is directly related to the ability of a nanoparticle to generate heat as the Joule effect is directly related to the magnitude of the electric field inside the particle.

The definition of the figures of merit we introduce in this article are based on the quantities E_{max} and E_{in} as explained in the following section.

Definitions of Fa and Jo. Let us define first a dimensionless parameter that quantifies the ability of a nanoparticle to enhance the electric field intensity in its surrounding medium:

$$Fa = \left| E_{\text{max}} / E_0 \right|^2 \tag{11}$$

where E_{max} is defined as the maximum electric field amplitude achieved in the medium surrounding the particle, for a given nanoparticle morphology and given illumination conditions. To simply refer to this number, we propose to call Fa the Faraday number. According to eq 7, in the case of a *dipolar sphere*, the Faraday number can be simply expressed as a function of the permittivities, or simply as a function of ξ :

$$F_{a} = |1 + 2\xi|^{2} = 9 \left| \frac{\varepsilon}{\varepsilon + 2\varepsilon_{s}} \right|^{2}$$
(12)

For a given material, this dimensionless parameter depends only on the nature of the surrounding medium (via ε_s) and the illumination wavelength λ .

The way it is defined, the Faraday number can be used to quantitatively compare different materials, different wavelengths, and different environments as well, for a given incoming electric field intensity E_0 . However, the incoming electric field is usually not what is controlled experimentally. One rather sets the light irradiance (power per unit area), which is not only proportional to the electric field intensity, but also involves the refractive index n_s of the propagation medium:

$$I = \frac{n_{\rm s}c}{2}\varepsilon_0 |\mathbf{E}|^2 \tag{13}$$

For this reason, if the question is to compare the near-field enhancement as a function of the surrounding medium, *at a fixed laser intensity*, one has to implement a prefactor $1/n_s$ in the definition (12) of Fa. This convention implicitly takes into account that the surrounding medium damps the electric field by a factor n_s . However, if the question is to compare the near-field amplification with a nanoparticle, compared to the case without nanoparticle, the prefactor is not appropriate and eq 12 can be used as it is.

In the same spirit, and according to eq 10, one can define a dimensionless parameter that quantifies the ability of the nanoparticle to enhance its inner electric field:

$$|E_{\rm in}/E_0|^2 = |\xi - 1|^2 = 9 \left| \frac{\varepsilon_{\rm s}}{\varepsilon + 2\varepsilon_{\rm s}} \right|^2 \tag{14}$$

However, this quantity is not yet a good quantifier of the ability of a metal to generate heat. Indeed, heat generation is not only related to the electric field intensity inside the particle, but also depends on the imaginary part of the permittivity of the material, and on the photon energy $\hbar\omega$. This can be clearly evidenced by writing the expression of the heat source density within the material:

$$q(\mathbf{r}) = \frac{\omega}{2} \varepsilon_0 \varepsilon'' |\mathbf{E}(\mathbf{r})|^2$$
(15)

For this reason, we rather define a dimensionless parameter that reads

$$Jo = \frac{e\varepsilon''}{n_s} |E_{in}/E_0|^2$$
(16)

This expression contains the imaginary part of the permittivity of the material ε'' and the photon energy *e* in eV, that is, $e = \hbar \omega / \hbar \omega_0$ with $\hbar \omega_0 = 1$ eV. One can also conveniently use the relation $e = \lambda_{\text{ref}} / \lambda$ where $\lambda_{\text{ref}} \approx 1240$ nm. We propose to call Jo the Joule number. In the definition of Jo, we have chosen to incorporate the prefactor $1/n_s$ by default (as opposed to the definition of Fa). Indeed, as explained earlier, the presence of this factor enables the comparison in different environments at a fixed light irradiance *I*, and not at a fixed incoming electric field amplitude E_0 , which is the common experimental approach when considering heat generation. The interest of using this prefactor will be manifest later on, in the discussion of Figure 3. Here is a list of other useful and equivalent expressions of Jo:

$$Jo = \frac{e\varepsilon''}{n_s} |\xi - 1|^2$$
(17)

$$=9\frac{\epsilon\varepsilon''}{n_{\rm s}}\left|\frac{\varepsilon_{\rm s}}{\varepsilon+2\varepsilon_{\rm s}}\right|^2\tag{18}$$

$$=\frac{\lambda_{\rm ref}\sigma_{\rm abs}}{2\pi V} \tag{19}$$

where σ_{abs} is the absorption cross section of the nanoparticle, V denotes the nanoparticle volume, and $\lambda_{ref} \approx 1240$ nm. The latter expression, derived by considering the relation $qV = \sigma_{abs}I$, highlights the relation between Jo and σ_{abs} , two quantities related to heat generation in plasmonics. The Joule number turns out to scale as the absorption cross section divided by the nanoparticle volume. This is interesting because the common approach rather consists in dividing σ_{abs} by the projected surface of the nanoparticle to obtain a dimensionless number quantifying the absorption efficiency. Our formalism suggests that a division by the nanoparticle *volume* makes more sense. This expression also enables the extension of the definition of Jo to any nanoparticle geometry, not only for spheres, as discussed in the last section of this Article.

At the plasmonic resonance, the expressions 12 and 18 of the Faraday and Joule numbers can be approximated by simpler expressions. Under resonance, the real parts of the denominators of Fa and Jo are supposed to be zero, which yields $\varepsilon' \approx -2\varepsilon_{\rm s} = -2n_{\rm s}^2$. Only the imaginary part therefore remains in the denominators and one ends up with these simplified expressions of Fa and Jo:

$$Fa(\lambda_{res}) \approx 9 \left| \frac{\varepsilon_{res}}{\varepsilon_{res}''} \right|^2 = 9 \left(1 + \left| \frac{\varepsilon_{res}'}{\varepsilon_{res}''} \right|^2 \right)$$
(20)

$$Jo(\lambda_{res}) \approx 9e \frac{n_s^3}{\varepsilon_{res}''} = 9e \frac{|\varepsilon_{res}'|^{3/2}}{\varepsilon_{res}''}$$
(21)

As stated in the introduction, the usual figure of merit in nanoplasmonics reads $-\varepsilon'/\varepsilon''$, which differs from the figures of merit we derived in eqs 20 and 21. Even though we end up with the same general trend (that is, ε' has to be large and ε'' has to be weak), our expressions appear as refined figures of merit, under plasmonic resonance. Out of plasmonic resonance, the simplified eqs 20 and 21 are no longer valid, and one has to consider the more general definitions of Fa and Jo, eqs 12 and 17, which are valid at any wavelength. Noteworthily, eq 21 tells us that ε'' has to be minimized even when considering heat generation. ε'' is yet related to loss and according to eq 15, one could have thought that a large value of ε'' could have been beneficial for the photothermal properties of nanoparticles, but it is not the case. While heat generation seems to be proportional to ε'' in eq 15, the inner electric field E_{in} is

Table 1. Dimensionless Numbers	Characterizing the Ability of	a Material to Enhance th	e Near-Field (Fa ⁰), ¹	Generate Heat (Joº),
along with the Corresponding Re	esonance Wavelengths $\lambda_{ m res}^{ m in}$ and	nd $\lambda_{\rm res}^{\rm out}$		

ref			$\lambda_{ m res}^{ m out}~(m nm)$	Fa ⁰	$\lambda_{ m res}^{ m in}~(m nm)$	Jo ⁰	$T_{\rm s}$ (°C)
16	gold	Au	528	19.6	507	6.32	1064
17	silver (Palik)	Ag	357	118	354	52.0	961
16	silver (J&C)	Ag	355	476	354	111	
18	aluminum (Rakic)	Al	140	1290	140	477	660
16	copper	Cu	585	15.2	538	2.65	1085
19	cobalt	Co	366	10.9	<200	>12	1495
19	chromium	Cr	289	10.6	<200	>11	1907
19	iron	Fe	337	9.38	<200	>11	1538
17	molybdenum	Mo	154	18.3	140	41.3	2623
19	manganese	Mn	380	9.82	<200	>9.2	1246
19	nickel	Ni	218	11.6	141	21.4	1455
19	palladium	Pd	223	13.3	<200	>21	1555
17	platinum	Pt	323	10.5	210	12.0	1768
17	rhodium	Rh	199	18.4	173	31.5	1964
17	tantalum	Та	735	11.8	640	2.45	3017
17	tantalum	Та	177	11.6	77	52.3	
19	titanium	Ti	274	11.2	<200	>13	1668
17	titanium nitride	TiN	566	12.0	488	5.55	2930
17	tungsten	W	159	14.2	131	25.6	3422
17	zirconium nitride	ZrN	467	28.6	437	16.6	2952
Omtical com	stants want taken from usfr	mana indiantad	in the first column	$T(^{\circ}C)$ is the m	altin a tanan anaturna	at atma asmbania n	*****

'Optical constants were taken from refrences indicated in the first column. $T_{\rm s}$ (°C) is the melting temperature at atmospheric pressure.



Figure 2. Spectra of the Faraday (a-c) and Joule (d-f) numbers for a large set of materials. Materials have been arranged in families: Plasmonic resonance out of the visible range (a, d), in the visible range (b, e), and the singular case of silver (c, f) where data have been plotted considering two distinct data sets (the optical constants of Johnson and Christy, and of Palik's handbook).

actually damped by a factor $|1/\varepsilon''|^2$, and hence the $1/\varepsilon''$ general dependence of Jo.

For a given material, the Faraday and Joule numbers depend only on λ and n_s . If one considers standard conditions where (i) the nanoparticle is illuminated at its plasmonic resonance wavelength ($\lambda = \lambda_{res}$) and (ii) in vacuum ($\varepsilon_s = 1$), one ends up with universal dimensionless parameters associated only to the nature of the material. Let us name Fa⁰ and Jo⁰ the values of Fa and Jo under these standard conditions. Table 1 draws up the values of standard Faraday and Joule numbers for most materials that have been investigated in plasmonics so far. The resonance wavelengths for Faraday and Joule numbers have been determined by calculating Fa and Jo spectra (using eqs 12 and 17) and interestingly, both resonance wavelengths differ in most cases. This is already an interesting observation, which is in direct relation with the well-known frequency shift between the near-field and far-field plasmonic resonances.^{20–22} In this table, as detailed above, the Faraday number Fa⁰ characterizes the ability of the metal to enhance the

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optical near-field when used in plasmonics and the value $Fa^0 =$ 9 is the lower limit corresponding to the absence of plasmonic resonance (see previous section). Hence, materials characterized by a Faraday number around 9 or below have poor plasmonic properties for near-field applications. For gold $Fa^0 =$ 19.0, which means that the occurrence of a plasmonic resonance in a gold nanosphere contributes to enhance the near field intensity almost by a factor of 2 compared to the static case (19 instead of 9). One can also notice that, while gold seems to be an efficient near-field enhancer ($Fa^0 = 19$), it does not seem particularly efficient for heat generation compared to other materials $(Jo^0 = 6.32)$, one of the lowest values of the table). Yet, gold is the most common material in thermoplasmonics. A promising material for thermoplasmonics that yields plasmonic resonance around the same range of wavelength seems to be ZrN. It features better Faraday and Joule numbers than gold ($Fa^0 = 28.6$ and $Jo^0 = 16.6$).

In parallel with Table 1, spectra of the Faraday and Joule numbers are plotted in Figure 2. These spectra enable the comparison of materials at given wavelengths (e.g., matching experimental constraints). Materials have been gathered in families that feature similar line shape profiles. Figure 2a,d gathers materials resonating in the UV. Interestingly, they are all quantitatively equivalent in the visible range, especially regarding their photothermal properties. A second family gathers materials undergoing a plasmonic resonance in the visible range (Figure 2b,e), and a third graph is dedicated to the particular case of silver.

Fa spectra are supposed to tend to 9 for large wavelengths (approaching the static case). The lines Fa = 9 are indicated in each graph as a solid horizontal black line. On the contrary, Jo spectra are not leveled down by any nonzero lower value at large wavelength. On the contrary, Jo numbers tend toward zero, which is consistent with the absence of heat generation with the static case. However, the main difference with the Fa line shapes is a strong heat generation enhancement at short wavelength (strong Jo values). This feature comes from the presence of the ω factor in the expression of Jo (eqs 15 and 17). In other words, this enhancement does not come from an increase of the absorption rate of the incoming photon, but rather stems from the fact that the involved photons have higher energies themselves at short wavelengths. This effect does not hold for the Faraday number, and the associated nearfield enhancement. On the contrary, at short wavelength, nearfield enhancement tends to vanish.

According to Table 1, silver appears to be a material leading to gigantic plasmonic resonance. However, numerical estimations of their plasmonics properties are usually not in accordance with experimental results. This discrepancy stems for metal sulfidation,^{23,24} which is difficult to control and strongly damps the plasmonic resonance. For this reason, it is hard to benefit from the outstanding plasmonic properties of silver, experimentally.²⁵ Studies of the plasmonic damping due to sulfidation of silver aroused interest this past decade. The shift of the resonance peak wavelength has been measured to be 65 nm after 36 h in contact with air, a shift attributed to the contamination from sulfur and the formation of AgS₂ on the nanoparticle surface.²³ In some circumstances, Ag nanoparticles can even feature a lower scattering yield than Au.²⁴

This unavoidable contamination results in another problem in the community: the reliability of the reported optical constants tables of silver. Although many data sets have been reported for the optical properties of silver, two main references are used when conducting numerical simulations with silver in plasmonics: the values of the optical constants reported by Johnson and Christy (henceforth referred to as $[\&C]^{16}$ and the values gathered in Palik's handbook.¹⁷ One of the reasons for their widespread use is that these data sets are tabulated over a wide wavelength range, covering the ultraviolet, visible and infrared. In Figure 2c,f, Fa and Jo spectra calculated using J&C's and Palik's tables are compared and a substantial difference can be observed. As stated in ref.,²⁶ small variation in the optical constants can be magnified several fold under plasmonic resonance, leading to inaccuracies in the modeling and interpretation of results. It is probable that the degree of sulfidation of the metal layer was not the same during the different series of experiments at the basis of these data sets. It is usually admitted that J&C values tend to overestimate the plasmonic response while Palik's values tend to underestimate it.²⁶ Moreover, Palik's data sets actually combine the work of four research groups using different sample preparation methods, which yields some inconsistencies. Jiang et al.²⁶ recently published a comprehensive review of the problem and proposed to re-evaluate the optical constants of silver measured so far. Note that new measurements of the optical constants of silver have just been reported by Yang et al.²

Aluminum is envisioned to be the ideal candidate for numerous applications in UV plasmonics.²⁸⁻³⁴ Indeed, aluminum exhibits a strong plasmon resonance in the ultraviolet (around 140 nm), similar to silver. Among all plasmonics materials considered, Al demonstrates the strongest near-field enhancement (Fa = 1288) and photothermal efficiency (Jo = 477). Unfortunately, Al suffers from the same problem as silver and oxidizes even more rapidly.¹⁴ However, the native oxide Al₂O₃ results in the formation of a passivation layer that prevents complete denaturation of the material.³ The permittivity of Al can be corrected in order to take into account oxidation using the Bruggeman effective medium approximation, as recently proposed by Knight et al.²⁹ Considering what happens for silver and aluminum, one would think the stronger the plasmonic resonance, the higher the oxidation rate. But the validity and the reason for such an unfortunate relation has not been established to our knowledge.

Beyond Au, Ag, and Al (the common plasmonic metals), Table 1 and Figure 2 also feature a wide variety of new materials that arose a substantial interest over the last 5 years. In particular, we also present Fa and Jo calculations related to the so-called refractory metals.³⁶ This adjective refers to materials that can sustain strong temperature increase, such as TiN, ZrN, W, Mo, and Ta. For this reason, a column listing the melting points of all the materials has been appended to Table 1. These materials have been proposed as plasmonic materials for recent high-temperature applications such as heatassisted magnetic recording (usually termed HAMR) or thermophotovoltaics.

Lastly, particular attention can be paid to the metal nitrides TiN and ZrN (and HfN to a lesser extent).³⁷ They have drawn attention for plasmonics applications, mainly promoted by the groups of Boltasseva and Shalaev. These refractory materials have been proposed to replace gold for applications in hightemperature plasmonics due to their high melting point. In particular, the groups investigated the near-field³⁸ and photothermal³⁹ properties of TiN in two recent publications. According to Figure 2, TiN and ZrN feature near-field and photothermal efficiencies similar to the case of gold, the most used material in plasmonics. On the one hand, ZrN exhibits a



Figure 3. (a–c) BEM simulations of the near-field maps of spherical Au, ZrN, and TiN nanoparticles, 20 nm in diameter. $\lambda = 522$ nm and $n_s = 1$. (d–f) Same simulations for nanoparticles in water ($n_s = 1.33$). (g) Table listing the heat power and near-field enhancement obtained by BEM numerical simulations, along with the three calculated figures of merit, for the case $n_s = 1$. (h) Same table for the case $n_s = 1.33$.

dramatic resonance around 460 nm that widely exceeds that of gold. On the other hand, the Joule number of TiN remains significantly different from zero at large wavelengths, while the Joule number of most materials rapidly drops to zero after their resonance. As a result TiN demonstrates a broadband heat generation in the visible region. These two observations partly explain the recent interest of metal nitrides in plasmonics. Another advantage of such composite materials is that their permittivities, and consequently their plasmonic efficiencies, can be varied depending on the relative contents of metal and nitrogen. For this reason, in ref 39, to conduct their numerical simulations, the authors did not use data sets from the literature. They measured the permittivities of their own TiN samples. Interestingly, the measured values of the permittivities of TiN are rather different from the permittivities of Palik's handbook, which suggests that data sets from handbooks and articles always have to be taken with care, especially with composite materials. Moreover, they have shown that the permittivity of TiN depends on sample annealing during material deposition, as annealing induces a change of the Ti/N stoichiometry. For instance, higher substrate annealing temperature $(800^{\circ} \text{ compared to } 400^{\circ})$ yields much better photothermal efficiencies.

As an illustration of the benefits of the Fa and Jo numbers, we compared the predictions provided by the figures of merits Fa, Jo, and $-\epsilon'/\epsilon''$ with the results of exact numerical simulations performed using the Boundary Element Method (BEM)⁴⁰ for three different materials, Au, TiN, and ZrN, and in different surrounding media, vacuum ($n_s = 1$) and water ($n_s = 1.33$). All the results are presented in Figure 3.

We chose to consider spherical nanoparticles, 20 nm in diameter, illuminated at a common wavelength $\lambda = 522$ nm. The Fa numbers are systematically quantitative indicators of the actual field enhancements at the nanoparticle vicinity. Indeed, columns Fa faithfully reproduces the maximum $|\mathbf{E}/\mathbf{E}_0|^2$ values observed in each figure (a–f), reported in the columns $|\mathbf{E}_{max}/\mathbf{E}_0|^2$ of the tables (g) and (h). Moreover, Jo numbers quantitatively reproduce the relative photothermal efficiencies from one nanoparticle to another (for instance, 19.1/5.15 \approx

4.13/1.12 \approx 3.7), and from one medium to another (for instance, 5.15/3.15 \approx 1.12/0.695 \approx 1.6). The values of $-\varepsilon'/\varepsilon''$, however, fail in quantifying the relative plasmonic efficiencies. In particular, the values have usually nothing to do with the photothermal efficiencies. For instance, $-\varepsilon'/\varepsilon''$ predicts that a 20 nm ZrN nanoparticle would feature the most efficient plasmonic resonance for n = 1 (2.63 > 1.58, 0.497), while it is actually the poorest heat generator (3.15 < 4.96, 5.15). The near-field enhancement efficiencies are, however, better revealed by $-\varepsilon'/\varepsilon''$ predicts that a ZrN nanoparticle should be more efficient than a Au nanoparticle (2.63 > 1.58), while they actually feature very similar near-field enhancements (19.3 and 20.2).

Note that Fa and Jo cannot be compared one with each other to determine, for instance, if a nanoparticle is a better heat generator or field-enhancer. First, such a comparison does not make sense as an electric field and a heat power do not have the same dimension. Second, there is a necessary arbitrariness in the definition Jo (though the factor e; see eq 17), which further explains why Jo numbers can be compared one with each other, but not with Fa numbers.

Simulations have been also conducted in a water environment (n = 1.33), where Fa and Jo remain good indicators of both the near-field enhancement and the photothermal properties. For instance, Fa and Jo succeed in predicting that the photothermal efficiencies of the ZrN and TiN nanoparticles get inverted in water. However, the values of $-\varepsilon'/\varepsilon''$ cannot predict this observation as such a figure of merit does not involve the refractive index of the surrounding medium (which can be yet dramatic).

Finally, a last interesting comment regarding the results presented in Figure 3 concerns the inner electric field amplitude of the nanoparticle immersed in water. One can see in Figure 3d-f that the presence of a water environment tends to strongly enhance the penetration of the electric field inside the nanoparticle (the interior of the nanoparticle is no longer black in images d-f), resulting in a pronounced photothermal effect. The values of Jo are indeed enhanced by



Figure 4. Calculated Fa (a) and Jo (b) numbers plotted as a function of the resonance wavelength of ellipsoids made of various materials (Ag, Au, Cu, Ta, TiN, and ZrN). Each wavelength of the graphs corresponds to a different aspect ratio of the ellipsoid. Specific nanoparticle (NP) aspect ratios are indicated above circle markers.

factors of 4-6 compared to the case n = 1. This heat generation enhancement due to the presence of a refractive environment has to be considered as a general rule in plasmonics and can be understood by considering the expression 21 of Jo. However, the near-fields do not feature such a dramatic enhancement once the nanoparticles are immersed in water, as unveiled by the Fa values and the BEM simulations.

The illustrative cases depicted in Figure 3 were meant to explain how Fa and Jo numbers can be used and what kinds of useful and quantitative information can be derived, without conducting any numerical simulation.

The quantities Fa and Jo are important because they stand for universal dimensionless parameters that account for the plasmonic potential of different materials. However, these numbers do not relate to the enhancement featured by any nanoparticle, as enhancements naturally depend on the nanoparticle morphology as well. So far, Fa and Jo provide quantitative information only for dipolar spheres. Hence, for their general use in nanoplasmonics, these enhancement factors have to be rather considered as reference values, basic capabilities, starting points to characterize a plasmonic material.

We shall now see how Fa and Jo can also be used to characterize the plasmonic response of nonspherical nanoparticles.

Case of Nonspherical Nanoparticles. As defined by eqs 11 and 16, the Faraday and Joule numbers can already be considered as a simple, yet compelling, refinement of the figure of merit $-\epsilon'/\epsilon''$. In this section, we shall develop a further refinement of the theory in the case of elongated nanoparticles (prolate ellipsoids). We chose to investigate ellipsoids first because there exists analytical expressions for such a geometry, and then because elongating a nanoparticle morphology is the common approach to red-shift a plasmonic resonance.

The definitions of Fa and Jo (eqs 11 and 16) can be adapted in the case of ellipsoids using Mie–Gans formalism,⁴¹ which provides simple analytical expressions. When the polarization of the incident light is along the axis j, the so-called plasmonic enhancement factor reads

$$\xi_j = \frac{1}{3} \frac{\varepsilon - \varepsilon_s}{\varepsilon_s + L_j(\varepsilon - \varepsilon_s)}$$
(22)

where

I

$$r_{j} = \frac{R_{1}R_{2}R_{3}}{\int_{0}^{\infty} \frac{du}{(u+R_{j}^{2})\sqrt{(u+R_{1}^{2})(u+R_{2}^{2})(u+R_{3}^{2})}}}$$

where R_1 , R_2 , and R_3 denote the radii of the ellipsoid along the principal axes j = 1, 2, 3. Note that the depolarization factors L_j satisfy the relation $L_1 + L_2 + L_3 = 1$. The new expressions of the Faraday and Joule numbers for an incident polarization along the j axis are⁴²

$$Fa = |1 + 3(1 - L_j)\xi_j|^2$$
(23)

$$Jo = \frac{e\varepsilon''}{n_s} |1 - 3L_j\xi_j|^2$$
(24)

The expression of Fa directly comes from the expression of the electric field outside the nanoparticle in the direction parallel to the polarization of the incoming electric field.⁴² The derivation of the expression of Jo is less direct. We actually used the expression of the electric field outside the ellipsoid at $(r,\theta) = (a,\pi/2)$.⁴² This electric field is tangential to the interface and equals the electric field \mathbf{E}_{in} inside the nanoparticle because of the continuity of the tangential component of the electric field. Equations 23 and 24 can be recast into

$$Fa = \left| \frac{\varepsilon}{\varepsilon_{s} + L_{j}(\varepsilon - \varepsilon_{s})} \right|^{2}$$
(25)

$$Jo = \frac{e\varepsilon''}{n_s} \left| \frac{\varepsilon_s}{\varepsilon_s + L_j(\varepsilon - \varepsilon_s)} \right|^2$$
(26)



Figure 5. Practical case based on the comparison of two nanoparticles made of Ta and TiN, featuring the same volume and same plasmonic resonance wavelength. (a) Map of the near-field enhancement of a TiN nanoparticle (aspect ratio r = 3.42, n = 1). (b) Map of the near-field enhancement of a Ta nanoparticle (aspect ratio r = 1.425, n = 1). (c) Plot of the dissipated heat power spectra for the two nanoparticles, and for a laser irradiance of 1 $\mu W \mu m^{-2}$. (d) Spectrum of the figure of merit $\varepsilon'/\varepsilon''$. (e) Spectra of the Faraday number. (f) Spectra of the Joule number.

Just like what we have done in the case of a sphere with eqs 20 and 21, one can define simpler close-form approximations of Fa and Jo close to the plasmonic resonance, characterized this time by $\varepsilon_s + L_j(\varepsilon' - \varepsilon_s) \approx 0$. Since $iL_j\varepsilon''$ remains in the denominators, the corresponding expressions read

$$Fa(\lambda_{res}) \approx \frac{1}{L_j^2} \left| \frac{\varepsilon_{res}}{\varepsilon_{res}''} \right|^2$$
 (27)

$$Jo(\lambda_{res}) \approx \frac{e}{L_j^2} \frac{n_s^3}{\varepsilon_{res}''}$$
(28)

For a sphere, since $L_j = 1/3$, one retrieves the factor 9 and the eqs 20 and 21.

We calculated Fa and Jo spectra for various materials and for various ellipsoid aspect ratios r, ranging from 1 to 8. Note that the calculations involve the choice of a specific aspect ratio but not of a specific volume, as Fa and Jo do not depend on the volume of the nanoparticle, in the dipolar regime. From these spectra, we determined the resonance wavelengths λ_{res} for each value of r, which enabled us to plot the Faraday and Joule factors as a function of the resonance wavelengths (Figure 4). These spectra differ from the spectra plotted in Figure 2, which are related to a spherical geometry, no matter the wavelength. Here in Figure 4, the aspect ratio of the nanoparticle is different at each wavelength of the line shapes, to make sure the nanoparticle is illuminated at its plasmonic resonance at any point of these graphs, in order to match what is naturally done experimentally.

For the sake of conciseness, only the materials that feature a resonance in the visible range have been represented (Ag, Au, Cu, Ta, TiN, ZrN). From these results, one can see that the relative efficiencies of two materials can change when modifying the aspect ratio, that is, the resonance wavelength. For instance, when ZrN seems to feature much better characteristics than gold and copper for short wavelengths, gold and copper do better as soon as the nanoparticles are elongated and the

resonance shifted toward the infrared, both regarding their photothermal and optical near-field properties.

Another important aspect evidenced in Figure 4 is the rate with which the enhancement factors at resonance increase when elongating a nanoparticle, that is, the slopes of the line shapes. While the spectra of Ag, TiN, and ZrN are slowly increasing with respect to the aspect ratio, Au, Cu, and Ta spectra feature a rapid increase, especially at short wavelength. Interestingly, in any case, the effect of elongating a nanoparticle is either a strong red-shift of the resonance with a small plasmonic enhancement, or a strong plasmonic enhancement with a reduced red-shift. The two features, strong near-field enhancement and substantial red-shift, are never observed at the same time. For instance, up to an aspect ratio of 5, the resonance of gold nanoparticles are mainly characterized by an increase of the electric field enhancement (of around 3 orders of magnitude for Fa), with a reduced red-shift. And above an aspect ratio of 6, the resonance starts to red-shift faster while the enhancement numbers remains in the same order of magnitude (~ 10^5 for Fa and 5 × 10^3 for Jo). This trend is even more obvious in the case of copper.

In any case, the modification in the slopes of $Fa(\lambda_{res})$ and $Jo(\lambda_{res})$ comes from a change in the slope of $\varepsilon''(\lambda)$. For instance, for gold, below $\lambda = 680$ nm, both ε'' and L_j are decreasing, which naturally leads to a steep increase of Fa and Jo (see eqs 27 and 28). However, while L_j keeps on decreasing after 680 nm, ε'' increases which slows down the increase of the plasmonic efficiencies as a function of the wavelength.

Let us illustrate the aspect of the formalism related to elongated shapes with a practical case. The results are gathered in Figure 5. We chose to investigate the plasmonic response of two nanoparticles made of different refractory materials, TiN and Ta. The nanoparticles have ellipsoidal shapes featuring the same volume (equivalent radius of 20 nm) but different aspect ratios so that the plasmonic resonance wavelength remains roughly identical (around 750 nm for the near-field resonances and 640 nm for the far-field resonances). The near-field maps and the dissipated powers (Figure 5a-c) have been computed using BEM. Let us see how these features can be predicted by the different figures of merit. $-\varepsilon'/\varepsilon''$ roughly predicts the heat power enhancement of the TiN nanoparticle compared to the Ta nanoparticle at 640 nm (albeit not in a quantitative manner). It fails, however, in predicting the near-field enhancement. It predicts indeed an inversion of the efficiency at 750 nm, which is not observed in the numerical simulations. In parallel, the Faraday and Joule numbers manage to reproduce the results of the numerical simulations. The 5fold enhancement of the heat generation of TiN compared to Ta is predicted by the values of Jo, and the near-field enhancement values 167 and 23 obtained by BEM simulations are close to the Fa numbers 202 and 25. The small discrepancy between 202 and 167 in the case of TiN is attributed to the fact that the maximum near-field enhancement observed in the near-field map (Figure 5a) can be underestimated due to the finite size of the meshing, which does not allow us to probe the electric field at arbitrarily short distance from the nanoparticle surface.

Note that the Faraday and Joule numbers are not meant to address the question of the effect of the nanoparticle size on the plasmonic resonance. First, in the nonretarded regime, the near-field enhancement is not dependent on the size of the nanoparticle, just like any sphere enhances the near-field by a factor of 9, no matter his size, in the steady state regime. For instance, the near-field enhancement of small nanorods only depends on the aspect ratio, not on the nanoparticle size. The amount of heat generation is, however, strongly dependent on the nanoparticle size. But the Joule number is not meant to consider this effect because this effect is trivial in the nonretarded regime: the heat generation is proportional to the nanoparticle volume. If the aim is to quantify heat generation and compare different nanoparticles of different sizes, then the absorption cross section is the proper parameter to be used, not the Joule number. As the Joule number is basically the absorption cross section normalized by the nanoparticle volume (see eq 19), Joule numbers are rather aiming at saying whether the nanoparticle bulk is efficiently involved in heat generation. For instance, a macroscopic metal particle will naturally yield much stronger heat generation compared to nanoparticles, but the nanoparticle volume will not be efficiently used as most of the particle's volume would stay in the dark and will not contribute to heat generation. This information will be given by the Joule number, not by the absorption cross section.

The formalism developed in this Article is aiming at introducing a convenient approach to quantify and discuss the plasmonic efficiencies of nanoparticles in the nonretarded regime. For large particles undergoing retardation effects, the relative efficiencies we have derived in this article may non longer hold. For instance, the comparison of the relative efficiencies of gold and titanium nitride was the subject of a recent article.³⁹ TiN was shown to exceed Au capabilities in the infrared, when considering the photothermal properties of nanodiscs, 180 nm in diameter and 30 nm thick. This is not predicted by our formalism (in particular not by the results related to Figure 4), because the response of such a large structure is affected by retardation effects. For large nanoparticles where retardation effects play a dominant role, other more sophisticated close-form expressions of ξ could be used to derive approximate expressions of the Faraday and Joule numbers.⁴³ But for complicated geometries, numerical

simulations are required. Indeed, Faraday and Joule numbers can still be defined and computed numerically for any nanoparticle morphology. Fa simply remains the maximum electric-field enhancement in the surrounding medium, which can be calculated numerically. The case of Jo is slightly different. The inner electric field $E_{\rm in}$ is no longer uniform within large nanostructures, making the definition (16) of Jo no longer consistent. However, Joule numbers can still be defined using eq 19 relating Jo and $\sigma_{\rm abs}$, which can be calculated numerically. Within the context of this article, which is mainly intended to introduce the Faraday and Joule numbers, we shall not further detail how they can be conveniently used in the retarded regime. This could be the subject of a forthcoming article.

CONCLUSION

To summarize, we introduced two dimensionless parameters, Fa and Jo, defined by eqs 12 and 17, which we termed Faraday and Joule numbers, aiming at quantifying and comparing the basic efficiencies of materials for plasmonics applications. At resonance, simplified expressions can be used, given by eqs 20 and 21. We explain how these metrics appear as a refinement of the common figure of merit $-\epsilon'/\epsilon''$ that has been used so far. The benefit of using Faraday and Joule numbers is many-fold: (i) they feature close-form expressions for spheres and ellipsoids and can be simply calculated without numerical simulations, in the nonretarded regime, (ii) they separately quantify two main effects in plasmonics: near-field enhancement and heat generation, (iii) they yield quantitative information, and (iv) they take into account the influence of the surrounding refractive index.

This Article was also the occasion to discuss practical examples, such a the comparison between gold and metal nitrides, and the comparison between TiN and Ta, two promising refractory materials.

Within this Article, we have restricted the discussion to a limited set of materials, but the number of possible systems that Fa and Jo could apply to is not restricted. In particular, we did not discuss materials such as gallium,^{44–46} yttrium,¹² alloys,⁴⁷ quantum dots,⁴⁸ metal oxides,⁸ and alkali metals like magnesium.¹¹ These are other families of materials undergoing an increasing interest in plasmonics.

The strong gain of interest for new materials in plasmonics is currently giving rise to a new branch of research in nanoplasmonics. We believe it is important to find a short appellation for this emerging and important area of research, just like *bioplasmonics, thermoplasmonics, molecular plasmonics,* and *quantum plasmonics* have been conveniently introduced this past decade. We propose to coin the term *heteroplasmonics* to describe the area of nanoplasmonics based on the use of materials that differ from the most common materials Au, Ag. This neologism is inspired from the denomination *heteroatom* in chemistry that relates to any atom that differs from the most common atoms (H and C) constituting organic molecules.

MATERIALS AND METHODS

Numerical simulations were conducted using the Boundary Element Method (BEM), via the MNPBEM Matlab work-package developed by Hohenester and Trügler.⁴⁰ Sphere and ellipsoid meshes were created using Blender and composed of 4582 vertices.

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Notes

The authors declare no competing financial interest.

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