Selective and Collaborative Optimization Methods for Plasmonics: A Comparison

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Abstract— In this paper, we optimize the size parameters of hollow nanospheres and nanoshells used in cancer photothermal therapy and we focus on two practical therapy cases: the visible range for shallow cancer and the near infrared for deep cancer. For this, we consider analytical models: the Mie theory for coated spheres. The investigated optimization methods are the Evolutionary Method (EM) and the Particle Swarm Optimization (PSO) which are based on competitiveness and collaborative algorithms, respectively. A comparative study is achieved by checking the efficiency of the optimization methods, to improve the nanoparticles efficiency.

1. INTRODUCTION

The biomedical application of plasmonic resonances of metal nanostructures, taking advantage of the acute interaction, between light and metallic objects, remains an open domain even if some recent experimental studies have been already devoted to applications. For instance, the first successes of cancer treatment using nanoparticle-based photothermal therapy (PTT) are encouraging for more investigation in this field to ensure strong and tunable surface plasmon resonance (SPR) for efficient heat conversion. Nevertheless, at our knowledge, up to now, no optimization method has been developed to improve the efficiency of these plasmonic structures, through the mastering of the nanoparticles shape and size.

The nanoshells and the hollow nanospheres are among the most commonly used nanoparticles for PTT. The nanoshells are made of a silica core coated with a thin gold shell while the hollow nanospheres look like a gold bubble. For PTT applications, the illumination of the nanostructure induces an elevation of temperature which is used to burn the cancer cells. The absorption band of these particles can be tuned by adjusting the thickness of the gold shell and the inner radius and thus would enable both strong scattering and absorption efficiency [1]. Therefore, they can be used as contrast agents with dual functions for imaging as well as therapy. In this study, the target is to maximize the electromagnetic absorption of either the nanoshell, or of the hollow nanosphere, computed using the Mie theory (coated sphere) [2], responsible for heating process in PTT. For this, two optimization methods are investigated.

The meta-heuristics used in this study are the Evolutionary Method (EM) which is based on competitiveness and the Particle Swarm Optimization (PSO) which is based on a collaborative search algorithm. Some modifications of these conventional methods were proposed [3, 4] to get faster convergence in the optimization of planar biosensor. The optimization of nanoparticles differs from the one of planar biosensor in terms of the mathematical properties of the model (different topology) — even if the best parameters should correspond in both cases to a plasmon resonance — and the target of the optimization (the maximum of absorbed intensity in the metal instead of the maximum of the reflected intensity). It should be mentioned that a problem of optimization in plasmonics is based on a complex model of interaction between light and matter, depending on many material and geometrical parameters, and therefore requires always the use of rapid optimization method. This paper is organized as follows: the second section presents the PTT using gold nanoshell, hollow nanosphere and other nanoparticles. In the third section, the optimization methods used in this study are briefly described. In the fourth section, simulation results in some commonly used experimental conditions are presented and discussed before concluding.

2. PHOTOTHERMAL THERAPY USING GOLD NANOPARTICLES

The basic concept of nanoparticle-based PTT is the combination of: gold nanoparticles (Au NPs) — which are biocompatible, nontoxic and easily conjugated to antibodies — and suitable light source to allow a safe delivery of heat to a tumor volume. The predominating benefit of such treatment is that it is both safe and efficient [5] as the healthy tissues are almost prevented from the heat damage, which is inevitable in other thermal treatments (microwave and RF ablation, magnetic thermal ablation, focused ultrasound therapy, etc.). Broadly two optical windows exist in tissue. The main one lies between 600 and 1300 nanometers (nm) and a second from 1600 to 1850 nm [6]. Most biological tissues have a relatively low light absorption coefficient in the visible (VIS) and near infrared (NIR) regions (600–1300 nm) known as the tissue optical window or therapeutic window. Over this window, organic molecules have limited absorption [5], whereas Au NPs absorb light millions of times stronger than the organic molecules. Almost all the absorbed light is converted to heat via nonradiative processes [7]. Therefore, cancer cells embedded with Au NPs receive sufficient heat to induce their necrosis via thermal effect with minimal damage to the surroundings. PTT in the visible region is suitable for shallow cancer (e.g., skin cancer) whereas for in vivo therapy of tumors under skin and deeply seated within tissue, NIR light is required because of its deep penetration due to minimal absorption and scattering-limited attenuation of the hemoglobin and water molecules in tissues in this spectral region. Therefore, in this paper, we are interested in the optimization of gold nanoparticles both in the VIS and NIR regions.

Among the Au NPs used in PTT: nanoshells, nanospheres, nanorods and hollow nanospheres. In 2003, Hirsch et al. [8] firstly demonstrated the NIR PTT both in vitro and in vivo using gold nanoshells. Nanospheres are shown to be of interest only for shallow cancer in the visible range [7]. While, in many experimental studies nanorods are shown to be more efficient than nanoshells and therefore require lower laser intensity for photothermal therapy [7]. Nevertheless, these studies consider only some samples of nanoshells (not optimized). For instance, some experiments [9] show that gold nanorods have optical cross-sections comparable to nanoshells, however, at much smaller effective size. Similarly, nanorods were found to exhibit higher absorption efficiency than nanoshells with the same volume of metal [10]. However, theoretical results show that much improved absorption efficiency could be obtained with nanoshells [11]. Regarding hollow nanospheres, no similar comparison was reported but the advantages of having spherical shape were demonstrated. In fact, most of Au NPs have sizes that are too large or shapes that are too complex for biomedical applications. The right size and shape are needed for effective delivery to locations of interest for detection, imaging, or PTT. In addition, the spectral bandwidth of the surface plasmon absorption should ideally be narrow for a better match with the laser wavelength. The breakdown of the symmetry of nanostructures produces different modes and thus broad spectrum absorption. Therefore, in the ideal case, nanostructures with narrow but tunable absorption band, small size, and spherical shape are preferred [12, 13]. Hollow nanospheres guarantees such tunable resonance of plasmon absorption at different wavelength ranging from VIS to NIR as they were synthesized with great precision and controlled dimensions [1].

In what follows, the purpose is to find the best parameters set (r and e) to maximize the absorbed density of electromagnetic power, through a more efficient method than the basic double loop on these parameters.

3. OPTIMIZATION USING EVOLUTIONARY METHOD AND PARTICLE SWARM OPTIMIZATION

In this section, brief overviews of the methods used to optimize the structure (inner radius r and shell thickness e of nanoshells or hollow nanospheres) for getting a maximal absorption $M(t)$ in the shell, are given. For the above mentioned reasons, in this study, the target is to maximize the electromagnetic absorption of objects with spherical symmetry enabling PTT in VIS and NIR, i.e., hollow nanosphere and nanoshell. Actually, under continuous illumination by a laser at wavelength λ_0, the absorbed density of power is a function the inner radius r and the thickness of gold e: $M(r,e) = \pi c \Im(\varepsilon)|\mathbf{E}|^2/\lambda_0$, with c the speed of light in vacuum, $\Im(\varepsilon)$ the imaginary part of the permittivity of the absorbing medium (gold), $\mathbf{E}$ the electric field in this medium which is produced by the illumination, and λ_0 the illumination wavelength. In thermal problems, $M(r,e)$ is the source term of the heat equation. The electric field absorbed in the investigated nanoparticle (dielectric spheres with Au coating or hollow gold shells) is computed using Mie theory [2, 11]. The purpose of the optimization is to find as quickly as possible the best parameters (r,e) to reach the target $\max(M(r,e))$. Therefore, the fitness function of the optimization is $M(r,e)$.

3.1. ANUHEM

Evolutionary Methods were first introduced by Schwefel in 1995 [14] and also, among all, applied to the resolution of inverse problem [15]. The evolutionary method investigated in this study is a modified evolutionary method: the Adaptive Non Uniform Hyper Ellistist Evolutionary Method (ANUHEM) [4]. The evolutionary scheme consists basically of four steps: initialization, recombination, mutation and selection. A first population of parameters $x(1) = (r_i, e_i)$, $(i = 1 \dots \mu)$, with μ "parents", is randomly generated and $M(x(1)) = M(1)$ is evaluated and then begins the evolutionary loop on generation (or step) t:

1. *Recombination* (or crossover): randomly extracted elements of the initial population are combined together to lead to a secondary population of λ elements. The quality of each element (inverse value of the fitness function in case of minimization problem) is used to weight each element, leading to a barycentric approach.
2. *Mutation*: these elements are randomly mutated through a non-uniform law and evaluated ($M(x(t)) = M(r_j, e_j) = M(t)$ with $(j = 1 \dots \lambda)$ is computed). The Non-Uniform law is $NU(T, b, t) = 1 - U(0,1)^{(1-t/T)^{b(t)}}$, where $U(0,1)$ is the Uniform Law in $[0,1]$, t is the generation (iteration step), T is the maximum of allowed generations for the process, $b(t)$ is the adaptive term determining the degree of non-uniformity of the fitness function and given by the ratio of the standard deviation of the population to the standard deviation (std) of the fitness function, and this, for each element of $x(t)$: $b(1) = 1$ and $b(t+1) = std(M(t))/std(x(t))$.
3. *Selection*: the μ best elements are selected (the μ bests of $\max_j(M(t))$). This step is highly *selective*.
4. The initial population becomes the selected one.

ANUHEM uses the non-uniform mutation that increases the search capability of the algorithm, and weighted recombination that enables faster convergence toward the best set of parameters, compared to other evolutionary scheme [4].

3.2. PSO and Adaptive PSO (APSO)

Particle swarm optimization (PSO) was first introduced by Kennedy and Eberhart in 1995 [16] and imitates the swarm behavior to search the best solution. The PSO is basically a *cooperative* method where the vector of parameters $x(t)$ at step t is considered as a particle. The searched parameters are therefore considered as particles of a swarm which communicate good positions to each other and adjust their own position and velocity $V(t)$ based on these best positions as following:

$$V(t+1) = \omega(t)V(t) + U_1 c_1(t)(p(t) - x(t)) + U_2 c_2(t)(g(t) - x(t)) \quad (1)$$

$$x(t+1) = x(t) + V(t+1) \quad (2)$$

where U_i $(i = 1, 2)$ are independent random uniform variables between 0 and 1, $p(t)$ is the particle best position at step t, $g(t)$ is the global best over previous generations, $\omega(t)$ is the inertial weight and $c_i(t)$ $(i = 1, 2)$ are the acceleration coefficients. Equation (1) is used to calculate the particle new velocity using its previous velocity and the distances between its current position and its own best found position, i.e., its own best experience $p(t)$ and the swarm global best $g(t)$. Then the particle moves toward a new position following Equation (2). Similarly to ANUHEM, the particles keep moving in this method until the stop criteria are met (similar stop criteria will be adopted in section 4). The success of PSO strongly depends on values taken by c_1 and c_2. Zhan et al. outlined the necessity of updating these parameters following the evolutionary state determined using the mean distance between all the particles and the best one [17]. The method is fully described in [17] and cannot be summarized here. APSO was efficiently applied to a set of test functions and an improvement of the convergence speed of this method was proposed in a previous study [18] by decreasing the impact of the particles getting out of the domain of the physically acceptable parameters.

4. RESULTS AND DISCUSSION

Firstly, the endogenous parameters related to the model, and the exogenous ones related to optimization methods are fixed. The hollow particles can be made in sizes ranging from 10–12 nm in radius (outer radius) and 3 nm in shell thickness with a precision of 0.6 nm [1]. For this we can consider hollow gold nanospheres and nanoshells having an inner radius within the range 5–50 nm

Table 1: Optimization of hollow gold nanosphere and silica-gold nanoshell absorption through the size control (inner radius: r and shell thickness: e) to maximize the absorption. The target is $M = \max(|E|^2)$ in the metal.

		$\lambda_0 = 633\,\text{nm}$		$\lambda_0 = 800\,\text{nm}$	
		hollow nanosphere	nanoshell	hollow nanosphere	nanoshell
Best solution	e,r (nm)	$r = 7$, $e = 3$	$r = 5.5$, $e = 3$	$r = 25.5$, $e = 3$	$r = 21$, $e = 3$
	M	$M = 103$	$M = 82.5$	$M = 149$	$M = 139$
Standard PSO	Success (%)	86.7%	79.7%	89.7%	84.6%
	Evaluations	285	320	278	325
APSO	Success (%)	98.8%	100%	100%	100%
	Evaluations	217	307	158	220
ANUHEM	Success (%)	100%	100%	100%	100%
	Evaluations	106	120	259	183

and a metal thickness 2–30 nm which is an ideal range for biological applications that require small particles to be incorporated into living cells. Two different wavelengthes are considered $\lambda_0 = 633$ nm in the VIS range and $\lambda_0 = 800$ nm in the NIR range; which correspond to the treatment of shallow cancer (the case studied is skin dermis with refractive index 1.55 [6]) and deep cancer (the case studied is subcutaneous fat with refractive index 1.44 [6]), respectively. The exogenous parameters used for ANUHEM are the size of the initial and secondary populations $\mu = 5$, $\lambda = 25$ (typically $5 \leq \frac{\lambda}{\mu} \leq 7$ is the most efficient as discussed in [4, 14]) and $T = 40$ [3]. For PSO and APSO, the population size is set to 20. $c_1 = 0.738$ and $c_2 = 1.51$ and ω is linearly decreased for PSO whereas the parameters are updated following the evolutionary state as mentioned in [17] for APSO. The same stop criteria are defined for all optimization schemes: the loops are interrupted if the distance between all particles/seeds ($x(t)$), at iteration t, is lower than 1 nm, or if the number of evaluations of the fitness function M exceeds 1000. Let us underline that if an approximation of the best solution is computed through a systematic double loop on r and e, 4592 evaluations are required with a discretization of 0.5 nm.

A classical test of efficiency of the optimization methods consists in repeating several realizations of the optimizations, and the success rate is defined by the percentage of realizations that succeed to find the best solution. Thousand realizations are done for both algorithms: the success percentage and the mean number of evaluations needed to converge are reported in Table 1, as well as the best parameters (r and e) that guarantee the maximal absorption.

Results show that the standard PSO fails to avoid local optima: about 15% of failure for the different cases (particles are trapped in local optima). Therefore, improved PSO like APSO (almost 100% of successful trials) should be used for further SPR optimization schemes. Comparing APSO to ANUHEM, we find that APSO is faster for the optimization of hollow nanosphere for treatment of deep cancer ($\lambda_0 = 800$ nm) and that ANUHEM is more interesting in the other cases. Consequently, both strategies of optimization could be retained for plasmonics more complex problems. Both methods enable rapid convergence to the global optimal solution and thus their efficiency is confirmed. The maximum local field absorption is obtained at a wavelength of 800 nm for an inner radius of 25.5 and 21 nm for hollow nanosphere and silica-gold nanoshell, respectively (same shell thickness of 3 nm). This result is consistent with the optimization of the absorption cross section [11]. Similar results are obtained in the VIS which show that optimized hollow nanospheres are slightly larger in size. However, they exhibit more absorbtion and then would be more recommended mainly as forming a uniform shell on the silica core is very difficult for small clusters [7, 12].

5. CONCLUSION

The absorption of gold nanoshell and hollow nanosphere in two practical cases (shallow cancer and deep cancer) by means of the Mie theory has been optimized. The optimized results enables a comparison between silica-gold nanoshell and hollow nanosphere, and show that hollow nanosphere are slightly larger in size but exhibits more absorbtion. The radius of hollow nanosphere is greater than this of the nanoshell for both VIS and NIR wavelengthes ranges, but it has better efficiency in NIR. The thickness of the shell is always 3 nm, despite the change of the inner material in the two configurations. Concerning the optimization methods, the selective ANUHEM and cooperative APSO have comparable performances and succeed to avoid local optima (unlike the standard PSO). For further applications (other wavelengths and/or tissues and other SPR schemes), these two optimization methods could be used to optimize more complex plasmonic structures, the number of required evaluations to reach convergence being at least one order of magnitude less than that required by systematic search.

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