Renewable Energy xxx (2017) 1–8

Contents lists available at ScienceDirect

Renewable Energy

journal homepage: www.elsevier.com/locate/renene

Colloidal plasmonic structures for harvesting solar radiation

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A R T I C L E I N F O

Article history:
Received 12 September 2017
Received in revised form
22 October 2017
Accepted 31 October 2017
Available online xxx

Keywords:
Metallic nanostructures
Solar radiation absorption

A B S T R A C T

Direct Solar Absorption Collectors explore the thermo-optical properties of fluids to convert solar radiation into thermal energy. Colloids of metallic nanoparticles have shown a great potential to convert solar radiation into thermal energy efficiently, because of the matching between the absorption peak of the localized surface plasmon resonance and the solar radiation spectrum. Recently, multilayered metallic nano structures have been broadly studied for Thermo-optical applications due to the possibility to tune the plasmon resonance next to the near infrared region. In this work, using a full-wave field numerical model, we study the solar absorption of metallic nanofluids composed of Solid structures (Sphere, Cube, Tetrahedral, Octahedral), Silica-based structures (Shell and Multilayered) and its elliptical versions. Although a large part of the metallic material is replaced for SiO_2 in the nanofluid composition of NanoShell (NS) and Multilayered (ML) structures, the values of solar radiation absorber coefficients are larger than the obtained with solid particles. Also, the quantity of metal is just 18% (NS) and 53% (ML) of the material necessary to fabricate colloids of solid particles. For the elliptical structures, the values of solar radiation absorber condition are larger than the obtained with spherical structures.

1. Introduction

Solar collectors are renewable energy technologies developed during the last decades, which explore the thermo-optical properties of fluids to convert efficiently solar radiation into thermal energy [1,2]. The most common type of solar thermal collector employs a black absorber surface to transfer heat to a fluid that is circulating in tubes embedded within or fused onto the surface [3]. Inserting nanoparticles (NPs) in the fluid, a change of its thermophysical properties is caused, with an efficiency improvement next to 5% in solar thermal collectors [4]. This kind of Nanofluids has found applicability in systems where a fast and effective heat transfer is necessary, such as industrial applications, cooling of microchips, microscopic fluidic applications, etc [5].

On the other hand, to improve the energy transfer efficiency, the solar radiation must be absorbed directly by the working fluid as proposed by the Direct Solar Absorption Collector (DSAC), which is a thermal device composed of a transparent glass box containing the nanofluid. For a nanofluid of water and aluminum nanoparticles, the efficiency of a DSAC can increase up to 10% in comparison with a typical flat-plate solar collector [6]. Also, for a DSAC containing silver nanofluid, its efficiency can achieve a maximum value of 90% [7].

The efficiency of the solar radiation absorption is given mainly because of the matching between the metallic NPs optical absorption and the solar radiation spectrum [8,9]. In the case of gold and silver NPs, by cause of the localized surface plasmon resonance effect at visible region, the absorption peak can be tuned between 400 nm and 1300 nm [10,11], such that is possible to manage the solar radiation absorption efficiency altering the NPs geometry.

We have reported previously that the absorption spectrum of metallic nano-ellipsoids (NE) is red-shifted relative to that of a spherical geometry, therefore, it is possible to achieve a solar weighted absorption coefficient close to the ideal condition, managing the aspect ratio of the NE [12]. Recently another study has explored gold nano-rods and nano-sheets for the same purpose [13].

Other plasmonic structures with similar red-shifted resonance peak are the Nano-Shell (NS) [14] and Multilayered structures (ML) [15]. A NS is composed of a core covered by a thin metallic layer, the material properties of both the core and the shell regions, strongly influence the optical properties of the NS. In the particular case of a Silica-NS, with SiO_2 core and a Gold or Silver shell, a strong coupling between charges inside and outside of the shell causes a charge separation and consequently a red-shift of the absorption spectrum

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https://doi.org/10.1016/j.renene.2017.10.112
0960-1481/

Please cite this article in press as: D. Rativa, L.A. Gómez-Malagón, Colloidal plasmonic structures for harvesting solar radiation, Renewable Energy (2017), https://doi.org/10.1016/j.renene.2017.10.112

up to near IR spectrum [16]. For example, a Silica-NS with a core of 60 nm and a Gold shell with a thickness of 50 nm and 2 nm has a LPSR peak at 650 nm and 1100 nm, respectively [17].

On the other hand, the ML structures are composed of a metallic core, coated with a thin silica layer, and finally surrounded by a thin metallic shell (ex. Au/SiO_2/Au) [15,18–21]. MLs work like optical condensers and the electromagnetic field in the centermost dielectric layer can be enhanced multiplicatively with the number of layers [22]. Furthermore, the resonance peak of elliptical NS and ML is red-shifted for the same reasons as reported for NE [12,18].

In this work, the influence of metallic NPs structures on the solar radiation harvesting of solar collectors is analyzed; The nanostructures studied are solids, shells, multilayered, and its elliptical versions. The numerical model and the 3D simulation space are discussed in the methods section, posteriorly the differences between the solar weighted absorption coefficients obtained for the nanofluids containing the selected structures are discussed. We would like to note that chemical preparations of colloids based on the structures studied in this work have been already reported in the literature, allowing its immediate application.

2. Methods

2.1. Numerical model

We have explored a full-wave time harmonic field theory for the computational model analysis, using the COMSOL Multiphysics 5.0 software, Electromagnetic Waves, Frequency Domain interface (EMW package, for subwavelength geometries).

The 3D simulation space has two main regions, the studied structures and a surrounded medium, as can be seen in Fig. 1. The surrounded medium is composed of two spherical regions: an embedding medium (H_2O) and a perfectly matched layer (PML). The radius of the embedding and the PML spheres were chosen depending on the NPs diameter, such that NPs size variation further would not affect the simulation results.

In the case of Solar Radiation (low-intensity regime), the time-harmonic Electric field within the domain satisfies Maxwell equations in the frequency domain [23]:

$$\nabla \times \mu_r^{-1}(\nabla \times \mathbb{E}) - \omega^2 \varepsilon_0 \mu_0 \left[\varepsilon_r - \mathbf{j}\frac{\sigma}{\omega \varepsilon_0}\right]\mathbb{E} = 0 \quad (1)$$

where μ_r, ε_r and σ are the relative permeability, permittivity, and con-ductivity of the medium, respectively.

As represented in Fig. 1, in our model, the incident light is $p-$polarized at normal incidence with the electric field E along the $x-$axis, propagating in the $+z$ direction. To model an unpolarized light source (solar radiation), the average of the calculations for E_0 linearly polarized along the long axis and the short axis of the particle has been carried out.

2.1.1. Permittivity particle size considerations

The bulk metal dielectric permittivity can be described by an analytical expression based on the broadly accepted model for metallic materials, given by Ref. [24]:

$$\varepsilon_{Bulk} = \varepsilon_\infty - \frac{1}{\lambda_p^2\left(1/\lambda^2 + i/(\gamma_k\lambda)\right)} + \sum_{j=1,2}\frac{A_j}{\lambda_j}\left[\frac{e^{i\varphi_j}}{\left(1/\lambda_j - 1/\lambda - i\gamma_j\right)} + \frac{e^{-i\varphi_j}}{\left(1/\lambda_j + 1/\lambda + i\gamma_j\right)}\right] \quad (2)$$

where $_\infty$ is the high-frequency limit dielectric permittivity, λ_p is the plasma wavelength, λ_j is the interband transition wavelength, γ_k is the damping in the direction k, γ_j is the transition broadening, φ_j is the phase and A_j is the dimensionless critical point amplitude [24,25].

In the case of metallic materials smaller than the mean free path of free electrons, the dielectric permittivity for metallic NPs that accounts for the size dependence is given by Ref. [16]:

$$\varepsilon_{NP}\left(\omega, L_{eff}\right) = \varepsilon_{Bulk}(\omega) + \frac{\omega_p^2}{\omega^2 + i\omega\frac{v_f}{L_\infty}} - \frac{\omega_p^2}{\omega^2 + i\omega\left(\frac{v_f}{L_\infty} + \frac{Av_f}{L_{eff}}\right)} \quad (3)$$

where ε_{Bulk} is the bulk dielectric function of the NP's material, ω is the angular frequency of the incident light, ωp is the plasma frequency, vf is the Fermi velocity, L∞ is the mean free path of the electrons, A is the dimensionless parameter (A = 1) and Leff is the reduced effective mean free path of the electrons [26]. The Silver and Gold parameters have been reported in several articles [27,28].

2.2. Nano-structure geometries

It is well-known that for particles smaller than 10 *nm*, the

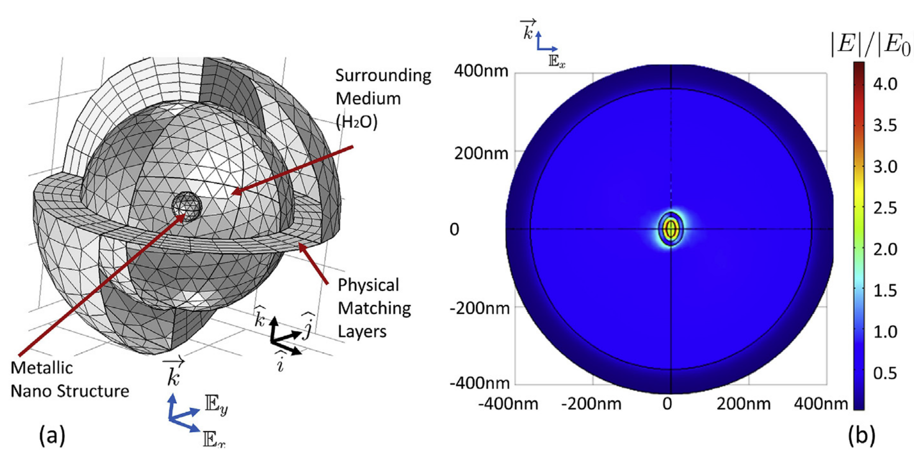

Fig. 1. (a) 3D Computational model regions composed of a Metallic Nanostructure studied, an embedding medium (H_2O) and a Perfectly Matched Layer; (b) Electric field maps, represented in colors corresponding to the electric field enhancement, $|E|/|E_0|$. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Please cite this article in press as: D. Rativa, L.A. Gómez-Malagón, Colloidal plasmonic structures for harvesting solar radiation, Renewable Energy (2017), https://doi.org/10.1016/j.renene.2017.10.112