Solar Energy 146 (2017) 503–510

Contents lists available at ScienceDirect

Solar Energy

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

Defects-assisted solar absorption of plasmonic nanoshell-based nanofluids

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ARTICLE INFO

Article history:
Received 27 September 2016
Received in revised form 14 January 2017
Accepted 8 March 2017
Available online 17 March 2017

Keywords:
Solar thermal conversion
Localized surface plasmon resonance
Core-shell
Plasmonic nanofluids

ABSTRACT

Plasmonic nanoshell-based nanofluids have recently been demonstrated to be promising candidates for efficient solar thermal conversion. During the nanoshells' fabrication processes, more often than not, only part of the dielectric core is covered by metals. However, there are few reports on how these particle defects affect the solar thermal conversion. In this paper, we find that the coverage defects of TiO_2/Ag nanoshells, instead of deteriorating, may enhance the solar absorption of nanofluids. The underlying mechanism mainly lies in the redshift of the symmetric localized surface plasmon resonance from the visible region for perfect nanoshells to the near-infrared in the presence of particle defects. The poor absorption of perfect nanoshells based nanofluids in the near-infrared is thus improved. The redshift can be quantitatively predicted and understood by an effective medium approach. This work opens a new route to enhance the solar thermal conversion of nanofluids by mediating the resonance absorption of composite nanoparticles via defects, and helps to deepen the understanding of plasmonic absorption properties of non-perfect nanoshells.

1. Introduction

Solar energy is renewable and abundant with the amount of 85000 TW impinging upon the earth, about 5000 times as high as the global energy consumption of 17.4 TW (Abbott, 2010; Mojiri et al., 2013). Therefore, solar energy is no doubt one of the most promising ways to tackle the increasing energy consumption need while relieving the environmental pollution problems and green house effects induced by traditional fossil fuels. Directly converting the sunlight into electricity via photovoltaic cells has been widely used all over the world. Nevertheless, only photons with energies larger than the semiconductor's bandgap can excite electron-hole pairs and contribute to the power output, and the excess energies turn into heat through thermalisation processes. Subsequently, the efficiency of photovoltaic cells is usually constrained by the Shockley-Queisser limit (Shockley and Queisser, 1961). Solar power plants, on the other hand, are not limited by the above issue. That is because the sunlight of all the spectrums can be absorbed and converted into heat, which is then used to drive thermodynamic cycles to generate electricities. This solar thermal technology has been commercialized as a cheaper and more efficient way compared with commercial silicon photovoltaic cells (Liu et al., 2016).

The key to the solar power plants with good performances lies in the efficient energy conversion from the solar power to the working fluid's thermal energy. Surface-based solar collectors, where surface coatings are employed to absorb the sunlight, are dominantly used in current solar power plants. With the assistance of state-of-the-art fabrication techniques and advanced simulation approaches, various structures have been proposed to absorb the sunlight from the whole visible to the near-infrared while limiting their thermal radiation via a low emissivity for the mid-infrared region (Celanovic et al., 2008; Sergeant, 2010; Wu et al., 2012; Wang and Wang, 2013; Cao et al., 2014; Lee et al., 2014). Nevertheless, the presence of thermal resistances due to conduction, interfaces, and convection leads to a large temperature difference between the surface coating and the working fluid, resulting in a high radiative heat loss, especially for high concentration solar thermal processes. This problem can be alleviated by employing volumetric solar collectors, where the solar energy is absorbed directly by the working fluid (Minardi and Chuang, 1975; Huang et al., 1979; Arai et al., 1984; Lu et al., 2011; Taylor et al., 2011b; Zhu and Zhang, 2012; Ladjevardi et al., 2013; Liu et al., 2013; Phelan et al., 2013; Luo et al., 2014; Xu et al., 2015; Chen et al., 2016; Gorji and Ranjbar, 2016; Li et al., 2016; Vakili et al., 2016), so that intermediate heat transfer processes associated with

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http://dx.doi.org/10.1016/j.solener.2017.03.024
0038-092X/

Nomenclature

A	spectral absorption coefficient
c	speed of light in vacuum
E	electric field, V/m
f	volume ratio of the shell compared with the whole composite nanoparticle
h	defect depth, m
H	magnetic field, A/m
I	solar intensity, W/m^2-nm
j	$\sqrt{-1}$
k	extinction coefficient
n	refractive index
Q	absorption efficiency
r	radius, m
v	volume ratio of nanoparticles compared with the water fluid

Greek symbols

α	polarizability
X	percentage of half-shell particles
ε	dielectric function
λ	wavelength, m
ω	angular frequency, rad/s
ξ	solar weighted absorption coefficient

Subscripts

abs	absorption
anti	antisymmetric mode
e	extraordinary wave
eff	effective
half	half-shell nanoparticles
inc	incident waves
o	ordinary wave
p	plasma frequency
perfect	perfect nanoparticles
s	shell
sym	symmetric mode
np	nanoparticles
0, 1, 2	numbers
x, y, z	Cartesian coordinates

entropy generation are avoided. However, common working fluids like water have a poor absorptance of the sunlight especially for the visible and near-infrared region, inhibiting the efficiency and wide applications of volumetric solar collectors.

Recently, dispersing metallic nanoparticles, such as Al, Cu, and Ag, in the base fluid has been proposed as a promising way to enhance its absorption capability (Tyagi et al., 2009; Otanicar et al., 2010; Kameya and Hanamura, 2011; Khullar et al., 2012; Lee et al., 2012; Lenert and Wang, 2012; Saidur et al., 2012; Phelan et al., 2013; Duan and Xuan, 2014; Chen et al., 2015; Zeng et al., 2016). The improved absorption coefficients are attributed to the excitation of localized surface plasmon resonances (LSPR), coherent oscillations of conduction electrons around the metallic nanoparticles due to the strong interaction with the incident light (Petryayeva and Krull, 2011). The electric fields near the particles are thus enhanced by orders of magnitude, leading to the efficient energy transfer from electromagnetic waves to the electrons inside the particles. Subsequently, the absorption capabilities of the working fluid are improved. The nanoparticles typically have a diameter of tens of nanometers, one order of magnitude smaller than the wavelength of incident sunlight; as a result, the dipolar mode which is characterized by localized resonant oscillations of charges in the formation of a dipole, plays a dominant role. An unpleasant consequence is that the absorption coefficient has only one narrow peak, especially when the optical loss of nanoparticles is small. Composite nanoparticles with dielectric cores covered by metal shells are promising alternatives to support high absorption coefficient in a broad wavelength region due to the hybridization of cavity and particle plasmons (Brandl et al., 2005). Recently, our co-authors (Xuan et al., 2014) experimentally demonstrated the broadband absorptance and good solar thermal conversion performances of TiO_2/Ag core-shell nanofluids. During the fabrication processes of core-shells, more often than not, only part of the TiO_2 core is covered by Ag. However, reports on how these particle defects affect the solar absorption properties of the nanofluids are rare.

In this paper, we investigate the solar absorption properties of TiO_2/Ag core-shell based nanofluids in the presence of particle defects. The Finite-difference time-domain (FDTD) approach is employed for predicting the absorption efficiency and field distributions of nanoparticles with arbitrary shapes due to its capabilities of dealing with complex nanostructures and obtaining spectral optical properties in a single run. The effective medium theory (EMT) will be used to assist the analysis. How the resonant absorption properties of nanoshells are mediated by defects and how to tune the resonant absorption peak will be discussed in detail. The solar weighted absorption coefficient is then calculated based on the extinction coefficients of nanoparticles and the base water, and how it is affected by particle defects will be presented later.

2. Methods

Before discussing the solar thermal conversion of nanofluids, we need to get the absorption efficiency of a single composite nanoparticle. The schematic of a single defective core-shell immersed in water is shown in Fig. 1. The radius of the core and the outer shell is r_1 and r_2, respectively. The defect length characterized by the distance from the outer shell to the core-shell crossover surface is h. The light is assumed to impinge along the y axis, perpendicular to the defect direction, with the electric field perpendicular to the defect direction, i.e., along the z coordinate, as shown in Fig. 1. The scenario of different directions of light propagation and electric fields will be discussed later. The classical electromagnetic theory via FDTD methods is used to calculate the optical properties of the composite nanoparticle. The absorption cross section can be calculated from the integral of the Poynting vector of the total fields over the surface surrounding the composite particle as (Bohren and Huffman, 2008):

$$C_{abs} = \frac{0.5 \iint Re(\vec{E} \times \vec{H}^{\dagger}) * d\vec{s}}{P_{inc}} \tag{1}$$

where $P_{inc}$is the power flux of the incident plane wave, and the absorption efficiency is defined as (Bohren and Huffman, 2008):

$$Q = \frac{C_{abs}}{\pi r_2^2} \tag{2}$$

The dielectric function of Ag is described by a Lorentz-Drude model $\varepsilon_{Ag} = 1 - \frac{F_0 \omega_p^2}{\omega(\omega + j\Gamma_0)} + \sum_{i=1}^{5} \frac{F_i \omega_p^2}{\omega_i^2 - \omega^2 - j\omega\Gamma_i}$, and the corresponding parameters can be obtained from (Rakic et al., 1998). The anisotro-