Photothermal Conversion Efficiency of Nanofluids: An Experimental and Numerical study

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Abstract: This work investigated experimentally the photothermal conversion efficiency (PTE) of gold nanofluids in a cylindrical tube under natural solar irradiation conditions, which was also compared with a developed 3-D numerical model. The PTE of gold nanofluids was found to be much higher than that of pure water, and increased non-linearly with the nanoparticle concentration, reaching 76.0% at a concentration of 5.8 ppm. Significant non-uniform temperature distribution was identified both experimentally and numerically, and a large uncertainty can be caused in the PTE calculation by using only one-point temperature measurement. A mathematical model was also established to calculate the solar absorption efficiency without knowing the temperature field within the nanofluids, which can be used to predict the theoretical PTE for nanofluids based on their optical properties only.

Keywords: nanoparticle; nanofluid; solar energy; photothermal conversion efficiency; direct absorption

30 Nomenclature

31	A	surface area exposed to solar radiation (m^2)
32		absorbance (-)
33	a_n	Mie coefficient to compute the amplitudes of the scattered field (-)
34	b_n	Mie coefficient to compute the amplitudes of the scattered field (-)
35	c	specific heat capacity ($\text{J}/(\text{kg} \cdot \text{K})$)
36	c_p	specific heat capacity at constant pressure ($\text{J}/(\text{kg} \cdot \text{K})$)
37	D	particle diameter (m)
38	E	spectral emissive power (W/m^3)
39	f_v	volume concentration (-)
40	h	convection heat transfer coefficient ($\text{W}/(\text{m}^2 \cdot \text{K})$)
41	I	radiative intensity (W/m^2)
42	k	thermal conductivity ($\text{W}/(\text{m} \cdot \text{K})$)
43	k_f	imaginary part of the complex refractive index of the based fluid (-)
44	L	optical depth (m)
45	m	mass (kg)
46		relative refractive index (-)
47	n	complex refractive index (-)
48		order of accuracy
49	q	heat flux (W/m^2)
50	Q	efficiency factor for Mie scattering (-)
51	Q_r	radiative heat source in heat transfer equation (W)
52	R	radius of cylinder tube (m)
53	r	radius in the integrating process (m)
54	$\hat{s}$	one specific direction which contains infinitesimal pencil of rays
55	T	temperature ($^{\circ}\text{C}$)

56	t	time (s)
57	U	uncertainty (-)
58	u	velocity (m/s)
59	x	characteristic size of nanoparticles (-)
60	<i>Greek symbols</i>	
61	β	extinction coefficient (m^{-1})
62	Φ	scattering phase function
63	ε	spectral emissivity (-)
64	η	efficiency (-)
65	κ	absorption coefficient (m^{-1})
66	λ	wavelength of light in vacuum (m)
67	σ	scattering coefficient (m^{-1})
68		Stefan-Boltzmann constant $= 5.670 \times 10^{-8} \left(\text{W}/(\text{m}^2 \cdot \text{K}^4) \right)$
69	Ω	solid angle
70	ρ	density (kg/m^3)
71	ψ_n	spherical Bessel function of order n
72	ξ_n	spherical Bessel function of order n
73	<i>Superscripts</i>	
74	-	average value
75	$\rightarrow$	vector quantity
76	<i>Subscripts</i>	
77	abs	absorption
78	amb	ambient
79	b	black body
80	ext	extinction
81	f	fluid
82	η	wavelength range
83	I	radiative intensity
84	i	direction number of light

85 *n* nanoparticle

86 *out* outlet

87 *p* particle

88 *sca* scattering

89 *s* scattering

90 *w* water

91 *Abbreviations*

92 ABE absorption efficiency

93 ARC advanced research computing

94 DASC direct absorption solar collector

95 DI deionized

96 FEM finite element method

97 GNP gold nanoparticle

98 MUMPS Multifrontal Massively Parallel Sparse

99 PTE photothermal conversion efficiency

100 RTE radiative transfer equation

101 SAR specific absorption rate

102 TC thermocouple

103 TEM transmission electron microscopy

104 UV ultraviolet

105

1 Introduction

The concerns over excessive use of fossil fuels and increasing environmental problems have accelerated the development of solar energy technologies (Sukhatme, 1997). However, the difficulties in efficiently collecting solar energy and converting it into useful energies, i.e., either electricity or heat, limit the extensive utilization of solar energy (Gupta et al., 2015). Most of current solar thermal collectors have the ‘tube-in-plate’ arrangements, which absorb solar energy on their surfaces and transfer heat to a working fluid circulating inside the tubes. For such an arrangement, the heat transfer is surface-limited, i.e., relying on the transfer of heat from a tube surface to the fluid inside. This would result in a large temperature difference between the fluid and the absorber especially for high temperature applications (i.e., solar thermal power plants) (Lenert and Wang, 2012), and limit the solar energy utilization efficiency.

The concept of volumetric solar energy absorption, i.e., certain materials are seeded in a working fluid to absorb solar energy directly within the fluid itself, was originated in 1970’s and coined as direct absorption solar collector (DASC) (Minardi and Chuang, 1975). In this concept, selective tube materials are employed to allow most of the solar energy to pass through the wall and into the fluid, but prevent the radiation leakage from the fluid, forming a ‘thermal trapping’ phenomenon (Arai et al., 1984). In this way, the highest temperature exists in the fluid and the overall conversion efficiency from solar energy to heat can be largely improved due to considerably reduced re-radiation heat loss.

The use of nanoparticles as effective absorption media is a recent development. It has been reported that adding a very small amount of nanoparticles into the base fluid (i.e. nanofluid) could improve the thermophysical properties of the base fluid, and enhance the radiative absorbing efficiency and improve the overall heat transfer rate due to their large specific surface areas (Wen et al. 2011; Vafaei and Wen, 2010a,b; Wen, 2012; Rahman et al., 2014). A range of nanoparticles including metal (such as Cu, Au, and Ag), metal oxide (such as TiO_2 , Al_2O_3) and carbon materials (Gan and Qiao, 2012; Hussain et al., 2005; Hwang et al.,

2014; Mock et al., 2002; Otanicar et al., 2010) have been investigated under laboratory (Lenert and Wang, 2012; Luo et al., 2014; Ni et al., 2015; Zhang et al., 2014) and natural sunlight conditions (Bandarra Filho et al., 2014; Neumann et al., 2013a, 2013b). Some results were very encouraging. For instance, the solar photothermal conversion efficiency of a 0.01% graphite nanofluid was found to be as high as 122.7% of that of a conventional surface absorbing collector (Luo et al., 2014). Some metallic nanoparticles such as gold and silver have also drawn wide attentions because of their Surface Plasmon Resonance effects (SPR) (Eustis and el-Sayed, 2006; Pérez-Juste et al., 2005). For these kinds of materials, the resonance frequencies of conduction electrons are usually in the visible-light spectrum, which is weakly absorbed by most of the heat transfer fluids but occupies nearly half of the total solar radiation energy (Thuillier et al., 2003). SPR-induced intensive absorption of radiative energy (i.e., even leading to vapor generation) has shown excellent photo-thermal conversion (Fang et al., 2013). Zhang et al. (2014) showed that a very low concentration of gold nanoparticles (i.e., mass concentration of 0.0028%) could increase the photo-thermal conversion efficiency (PTE) of the base fluid by 20%, and reached an impressive specific absorption rate (SAR) as high as ~10 kW/g under laboratory conditions. In another study conducted outdoor, up to 144% enhancement in the stored solar thermal energy was obtained for 6.5 ppm silver nanoparticle-based direct absorption under natural sunlight conditions (Bandarra Filho et al., 2014). However, it shall be noted that only one temperature was used to represent the bulk temperature in most of the published work (He et al., 2013; Kasaeian et al., 2015; Ladjevardi et al., 2013; Tyagi et al., 2009; Yousefi et al., 2012), and a uniform temperature distribution assumption was used to calculate the energy efficiency, neglecting the temperature difference within the fluid. Considering the non-linearly reduced radiative intensity along the depth of the absorbing fluid, there shall exist large temperature non-uniformity in the fluid, neglecting which may lead to inaccurate calculations for the PTE and disguise some key parameters (such as the optical depth) in optimizing the collector design.

Quite a few studies (Hordy et al., 2014; Kabeel and El-Said, 2014; Khullar et al., 2014; Lenert and Wang,

2012; Tyagi et al., 2009) have built numerical models to simulate the radiative and heat transfer processes in the nanofluids. Unfortunately, most of these simulation studies were based on the ideal solar spectrum, and ignored that the spectral emissive power distribution is affected by the atmosphere's absorption, especially in the infrared spectrum. As the radiation properties of nanoparticles are highly spectrum-dependent, any numerical work should consider the solar spectrum associated with realistic experimental conditions. A comprehensive theoretical method, without the need of calculating the temperature field within the fluid, to predict the photothermal conversion efficiency directly based on the nanoparticle's basic physical properties with respect to particle loadings and optical depth has yet to be established.

To address these issues reviewed above, a detailed investigation into the photothermal conversion characteristics of gold nanoparticle dispersions was conducted both experimentally and numerically. Gold nanoparticles were synthesized via a one-pot reaction, and the experiments were performed under natural sunlight conditions with multiple-points temperature measurements. A 3-D mathematical model was developed to simulate the direct solar absorption with nanofluids followed by a parametric study of the influence of particle concentration, solar radiation intensity and receiver geometrical parameters on the solar photothermal conversion efficiency. A new method to theoretically predict the photothermal conversion efficiency of nanoparticle dispersions was proposed according to the radiative transfer equation.

2 Experimental preparation

2.1 Gold nanoparticle dispersions formulation

In this study, a one-step method (Chen and Wen, 2011) was used to synthesize gold nanoparticle dispersions with different nanoparticle concentrations and sizes, as shown in **Table 1**. A typical procedure for CASE 6 in **Table 1** is introduced here. 2.5×10^{-7} mol HAuCl_4 was dispersed into 50 ml DI water in a three-necked flask under heating. A magnetic blender was used to stir the liquid until the attainment of boiling. Boiling lasted for about 10 min, and then 50 ml 1×10^{-5} mol/L sodium citrate was added into the gold

chloride acid solution. The mixed solution turned dark blue within 30 seconds, and the final color became wine red after being heated for an additional 20 min. The shape and size of gold nanoparticles for CASE 6 were characterized by a transmission electron microscopy (TEM), as shown in **Fig. 1a**. The UV-Vis absorbance of the gold nanofluids was checked every week, and the peak absorbance was almost the same over a period of two months, indicating that the gold nanofluids maintained good stability (Amiri et al., 2016, 2015). Gold nanofluid produced from CASE 6 in **Table 1** was diluted into sample fluids with different concentrations, which were used for the experiments below without further purification and separation.

A UV/Vis spectrophotometer (UV-1800 SHIMADZU) was applied to measure the absorption spectrum of the nanoparticle dispersions at different concentrations. As shown in **Fig. 1b**, due to strong localized surface plasmon resonance effect of gold nanoparticles in the visible light range (Zhang et al., 2014), an obvious absorption peak was found at the wavelength of 526 nm for all the dispersions, which coincided with the TEM results where the average size of the gold nanoparticles was about 20 nm. According to the Beer-Lambert Law (also known as Beer's Law) (Modest, 2003), expressed by Eq. 10 below, a strictly linear relationship exists between the absorbance and the concentration of the gold nanofluids, as shown in the inset of **Fig. 1b**.

2.2 Experimental setup

The experimental system in this study is shown in **Fig. 2**. The tubes in the experiments were custom-made from high temperature resistant quartz glass. The tube contained a vacuum interlayer to reduce the impact of convection heat loss to the ambient surroundings as much as possible. The sample fluids were placed in the inside-tube with a diameter of 25 mm and length of 300 mm. The outside-tube had a diameter of 60 mm with two small-bore pipes, which were used to fix the thermocouples.

A data acquisition system composed of a data logger (Agilent 34970A) linked to a PC under LabVIEW environment was used to monitor the temperature variations of the tested gold nanofluids and realize data display and storage. As shown in **Fig. 2b**, three type T thermocouples (Omega TT-T-40-SLE) with a

measurement uncertainty of $\pm 0.5\text{ }^{\circ}\text{C}$ were positioned evenly in the bottom, middle, top of the sample fluids along the depth corresponding to the light direction, and another two thermocouples were applied to measure the air temperature in the tube and the ambient temperature, respectively. A solar radiation intensity sensor with a measurement uncertainty of 2.0% was employed to measure the solar intensity, whose data was also recorded by the PC. In the experiments, the tubes were positioned perpendicularly to the sunlight to ensure the maximum solar absorption and the solar flux was measured by a solar radiation intensity sensor.

3 Experimental results and analysis

3.1 Temperature variation

Example temperature variation curves of gold nanofluids and DI water under varying natural sunlight are shown in **Fig. 3a**. A slow temperature increase in DI water was observed, and the solar intensity (I) varied from about 400 to 700 W/m^2 . Clearly the temperature variations of both DI water and nanofluids lag behind, but gold nanofluids exhibit much more rapid temperature increase than DI water under the same solar radiation conditions. For example, the bulk temperature was increased by $\sim 21\text{ }^{\circ}\text{C}$ after 60 minutes' solar radiation for the gold nanofluid with a concentration of 5.8 ppm, more than three times of the temperature rise of DI water. Here the average temperature from three thermocouples, i.e., $\bar{T} = (T_{TC1} + T_{TC2} + T_{TC3})/3$, was used to represent the bulk fluid temperature.

To reveal the possible temperature difference inside the fluid, **Fig. 3b** shows the temperature profiles of three thermocouples for 5.8 ppm gold nanofluid and DI water respectively under the same condition as that in **Fig. 3a**. A relatively large temperature difference was observed for the gold nanofluid, i.e., a maximum temperature difference of $2.6\text{ }^{\circ}\text{C}$ for gold nanofluid after 28 minutes' solar radiation, but for DI water, the maximum temperature difference was relatively small, i.e., less than $0.5\text{ }^{\circ}\text{C}$. Considering the potential large temperature difference within the gold nanofluid, as will be revealed by the numerical model below, the location of the thermocouple would affect the calculated PTE significantly if only one point temperature was

measured in the experiment.

Fig. 3c shows an example of the influence of solar intensity variation on the PTE for 0.72 ppm gold nanofluid. Under constant solar radiation, the fluid temperature increased smoothly and reached a steady state after two hours' illumination; but for varying solar intensity (i.e., cloudy day) with the same nanofluid, its temperature rise exhibited a continuously changing tendency, which followed the pattern of the solar intensity variation. Generally, salient temperature difference among the three thermocouples can be observed under both constant and varying solar intensities, being larger for a higher solar intensity. The non-uniform temperature distribution and its effects on the solar efficiency will be discussed further in **section 5**.

3.2 Photothermal conversion efficiency and specific absorption rate

The photothermal conversion efficiency (PTE) is conventionally defined as the ratio of the internal energy increase of the fluid to the total incident solar radiation:

$$\eta = \frac{(c_w m_w + c_n m_n) \Delta T}{IA \Delta t} \approx \frac{c_w m_w}{IA} \cdot \frac{\Delta \bar{T}}{\Delta t} \quad (1-a)$$

where $\Delta \bar{T}$ is the average temperature increase ($\Delta \bar{T} = (\Delta T_{TC1} + \Delta T_{TC2} + \Delta T_{TC3}) / 3$). Comparing with the base fluid, thermal energy stored in the gold nanoparticles is negligible owing to its extremely low concentration, i.e., a maximum of 5.8 ppm in volume (0.01% in mass). Here the total energy input from the Sun was used without considering the reflection from the glass tube. It should be noted that this definition of PTE only considers the increase of the internal energy, and neglects the contributions from latent heat (i.e., due to evaporation) and heat losses due to radiation and convection, which were relatively small at low temperature applications as in this work. Consequently we used the conventional definition of PTE for the purpose of comparison. Based on the standard error analysis method (Moffat, 1988), the uncertainty for the photothermal conversion efficiency can be expressed as:

$$\frac{U_\eta}{\eta} = \sqrt{\left(\frac{U_T}{\Delta T}\right)^2 + \left(\frac{U_I}{I}\right)^2} \quad (1-b)$$

To quantify the capability of nanoparticles in absorbing solar energy, the specific absorption rate (*SAR*) is employed (Bandarra Filho et al., 2014):

$$SAR = \frac{(c_w m_w + c_n m_n) \Delta \bar{T}_n - c_w m_w \Delta \bar{T}_w}{m_n \Delta t} \quad (2-a)$$

The uncertainty for *SAR* can be expressed as:

$$U_{SAR} = U_T \sqrt{\left(\frac{c_w m_w + c_n m_n}{m_n \Delta t} \right)^2 + \left(\frac{c_w m_w}{m_n \Delta t} \right)^2} \quad (2-b)$$

The calculated PTEs with the measurement uncertainties under two different solar intensities are shown in **Fig. 4**, which is in general similar to the previous studies (Bandarra Filho et al., 2014; Zhang et al., 2014). The PTE reaches 45.5% even at a relatively low concentration (0.36 ppm), increased by 163% comparing with the base water (17.3% at $I = 950 \text{ W/m}^2$). The highest PTE of gold nanofluids reaches 73.6%, which is more than 4 times of that of DI water and more promising than what was found in previous studies (Luo et al., 2014; Parvin et al., 2014; Zhang et al., 2014). The PTE increases rapidly under low particle concentrations and approaches asymptotically to a constant value when the concentration becomes larger than a certain value (i.e., 1 ppm for $I = 600 \text{ W/m}^2$). A lower PTE value (i.e., 10% smaller) is found for the high solar intensity case, which should be ascribed to an increased heat loss. **Fig. 4** also shows that *SAR* decreases rapidly with the increasing concentration when the concentration is below 1 ppm, and the highest *SAR* reaches 2.715 kW/g at a concentration of 0.36 ppm for $I = 950 \text{ W/m}^2$, which is in the broad range of previous studies (Bandarra Filho et al., 2014; Zhang et al., 2014). Further investigation with numerical results will be conducted regarding to PTE and *SAR* in **section 5**.

4 Numerical model of solar absorption with nanofluids

4.1 Solar radiation and Mie scattering theory

In order to get a better understanding of radiative heat transfer in gold nanofluids, a numerical model was built in this work. Real solar irradiation profile was employed based on the ASTM G173-03 Reference Spectra

(Gueymard, 2004). As shown in **Fig. 5a**, the solar irradiation reaching the ground is distinctly different from that at the top of atmosphere, especially for spectral emissive power in the infrared region due to intense absorption by H₂O and CO₂ in the atmosphere. The result from integrating the spectral emissive power with the wavelength shows that nearly 99% of solar radiation energy at the sea level exists in the wavelength range of 0.2~3 μm . Because it occupies nearly 43% of the total solar radiation power in the infrared region, as shown in the inset of **Fig. 5a**, considering the actual solar spectrum on the ground becomes essential for solar thermal applications. For simplification purpose, spectral emissive power for the sun ($T=5762$ K) and nanofluid ($T=303$ K) was calculated in different wavelength ranges separated at the wavelength of 3 μm (see in **Fig. 5b**); Solar irradiation power mainly exists in the wavelength range below 3 μm with a peak at 480 nm, while for nanofluid at 303K, most of the radiation power exists in the wavelength range beyond 3 μm . The calculation method adopted was similar to the one proposed by Lenert et al. (Lenert and Wang, 2012).

In the present model, the characteristic size in the radiative transfer equation is calculated as $x_\lambda = \pi D / \lambda$, where D represents the diameter of the nanoparticles. In our experimental study, the diameter of the gold nanoparticles is about 20 nm, as characterized by TEM in **Fig. 1a**. It is appropriate to use simplified equations, i.e., the Rayleigh scattering approximation (Bohren and Huffman, 1983), to calculate the absorption coefficient, since the diameter of the suspended particles in the experiments are much smaller than the wavelength of irradiation ($x_\lambda \ll 1$). The original Mie scattering equations (Modest, 2003) are preferred to identify the optical properties for spherical nanoparticle suspensions in order to obtain detailed scattering parameters, such as the efficiencies for scattering, absorption, backscattering, averaged absolute-square E-field. The Mie scattering equations can be described by:

$$a_n = \frac{m\psi_n(mx)\psi'_n(x) - \psi_n(x)\psi'_n(mx)}{m\psi_n(mx)\xi'_n(x) - \xi_n(x)\psi'_n(mx)} \quad (2-a)$$

$$b_n = \frac{\psi_n(mx)\psi'_n(x) - m\psi_n(x)\psi'_n(mx)}{\psi_n(mx)\xi'_n(x) - m\xi_n(x)\psi'_n(mx)} \quad (2-b)$$

$$Q_{sca}(\lambda) = \frac{2}{x^2} \sum_{n=1}^{\infty} (2n+1) \left[|a_n|^2 + |b_n|^2 \right] \quad (2-c)$$

$$Q_{ext}(\lambda) = \frac{2}{x^2} \sum_{n=1}^{\infty} (2n+1) \text{Re}(a_n + b_n) \quad (2-d)$$

where the functions $\psi_n(x)$ and $\xi_n(x)$ are spherical Bessel functions (Modest, 2003) of order n ($n=1, 2, \dots$) and the primes refer to the derivatives with respect to the argument, and m represents the ratio of refractive indexes, calculated by:

$$m = \frac{n_{particles}}{n_{fluid}} \quad (3)$$

where $n_{particles}$ and n_{fluid} are the complex refractive index (Babar and Weaver, 2015; Hale and Querry, 1973; McPeak et al., 2015) of gold and based fluid relative to the ambient medium, respectively. Considering relatively low concentrations of nanofluids employed in solar thermal applications, particles should absorb and scatter the light independently according to the scattering map (Modest, 2003). With such a consideration, the absorption coefficient can be calculated from the equation below:

$$\kappa(\lambda) = \kappa_p(\lambda) + \kappa_f(\lambda) = \frac{3\pi}{2} \frac{f_v Q_{abs}(\lambda)}{D} + \frac{4\pi k_f(\lambda)}{\lambda} \quad (4)$$

4.2 Radiative transfer equation and heat transfer equation

The property of spectral intensity can be described simultaneously by the radiative transfer equation, known as RTE (Modest, 2003):

$$\hat{s} \cdot \nabla I_\eta = \kappa_\eta I_{b\eta} - \beta_\eta I_\eta + \frac{\sigma_{s\eta}}{4\pi} \int_{4\pi} I_\eta(\hat{s}_i) \Phi_\eta(\hat{s}_i, \hat{s}) d\Omega_i \quad (5-a)$$

$$\nabla \cdot q_\eta = \kappa_\eta \left(4\pi I_{b\eta} - \int_{4\pi} I_\eta d\Omega \right) \quad (5-b)$$

$$\kappa_\eta = \beta_\eta - \sigma_{s\eta} \quad (5-c)$$

where I_η represents the radiative intensity in the wavelength range $\lambda_{\eta_1} \rightarrow \lambda_{\eta_2}$ in the direction $\hat{s}_i$, $I_{b\eta}$ is the re-emission of nanofluid, $\Phi_\eta(\hat{s}_i, \hat{s})$ is called the scattering phase function and describes the probability

that a ray from one direction $\hat{s}_i$, will be scattered into a certain other direction $\hat{s}$, κ_η , β_η and σ_η are the absorption, extinction and scattering coefficients, respectively. Spectral radiative heat flux q_η can be obtained by integrating the radiative intensity with the solid angle Ω .

Transient heat transfer equation is shown as:

$$\rho c_p \frac{\partial T}{\partial t} + \rho c_p \vec{u} \cdot \nabla T + \nabla \cdot \vec{q} = Q_r \quad (6-a)$$

$$\vec{q} = -k \nabla T \quad (6-b)$$

$$Q_r = -\int_0^\infty q_\eta(\lambda) d\lambda \quad (6-c)$$

The boundary and initial conditions are shown below:

$$-\vec{n} \cdot \vec{q} = \varepsilon \sigma (T_{amb}^4 - T^4) + h(T_{amb} - T) \Big|_{\text{contact_air}} \quad (7-a)$$

$$T_{t=0} = T_i \quad (7-b)$$

where h is the convective heat transfer coefficient at the mouth of the tube, whose contribution to the result is small and a typical value of $15 \text{ W}/(\text{m}^2 \cdot \text{K})$ is used in this work. As the concentration of the nanofluids here is relatively low (i.e., a maximum of 5.8 ppm), the change in the thermal conductivity and viscosity of the nanofluids can be safely neglected.

4.3 Predicted solar absorption efficiency

For the nanoparticles used in this study, scattering contribution can be neglected according to the Mie scattering theory. Furthermore, the radiative equations can be simplified as a 1-D transfer process. Based on these assumptions, an analytical solution for Eq. (6-a) can be obtained:

$$E_\lambda(L) = E_{\lambda,(y=0)} e^{-\beta_\lambda L} + E_{bb,\lambda} (1 - e^{-\beta_\lambda L}) \quad (8)$$

where E represents the spectral emissive power. Black body re-emissive radiation beyond $1.1 \mu\text{m}$, which is the upper limit of our UV-Vis spectrophotometer, can be neglected due to the small intensity of re-emission, as shown in **Fig. 5b**. Coupled with Eq. 5, Eq. 9 can be further simplified as:

$$-\log\left(\frac{E_{out}(\lambda)}{E_0(\lambda)}\right) = \beta_\lambda \cdot L \cdot \log_{10} e = \left(\frac{3\pi}{2} \frac{Q_{abs}(\lambda)}{D} \cdot \log_{10} e\right) \cdot f_v \cdot L = A(\lambda) \quad (9)$$

Eq.10 represents the analytic derivation process of the famous Beer-Lambert Law (Modest, 2003). With these assumptions, a new method is proposed to evaluate the total absorption efficiency (ABE) for a given nanoparticle concentration and optical depth, which should be the theoretically maximum photothermal conversion efficiency:

$$\eta(L, f_v) = \frac{\int_{0.2\mu m}^{3\mu m} E_0(\lambda) \left(1 - 10^{-A(\lambda) \frac{L}{L_0}}\right) d\lambda}{\int_{0.2\mu m}^{3\mu m} E_0(\lambda) d\lambda} = \frac{\int_{0.2\mu m}^{3\mu m} E_0(\lambda) \left(1 - e^{-\kappa(\lambda, f_v)L}\right) d\lambda}{\int_{0.2\mu m}^{3\mu m} E_0(\lambda) d\lambda} \quad (10)$$

Further investigation will be discussed in the next section together with experimental results.

4.4 Solution methodology

A high-order algorithm has been used to solve Eqs. (3) ~ (5) and (11) to calculate coefficients related to the optical properties for nanofluids and photothermal conversion efficiency in Matlab, similar to the one described by Kluczyk (Kluczyk and Jacak, 2016). It should be noted that obtaining an analytical solution to Eqs. (6) ~ (8) is extremely difficult as the 3-D transient heat transfer equations coupled with the transient RTE equations are complicated partial differential equations. A finite element method (FEM) powered by COMSOL Multiphysics was employed to solve these equations numerically. A predefined Heat Transfer with Radiation in Participating Media equations (Modest, 2003) together with user defined functions (radiative transfer equation) were used to describe the thermal and radiative energy transfer processes. The discretization of the computational domain was conducted using a built-in non-structured meshing COMSOL algorithm. The maximum element size inside the nanofluid was chosen as 0.2 cm, and the maximum size was chosen as 0.05 cm for the surface where the radiative and convective heat loss occurs. Before the simulation, various mesh numbers and time steps were tested for the independence verifications. Non-structured mesh was used, which consisted of 110342 domain elements, 5862 boundary elements and 320 edge elements. For the transient

model, the time-step was chosen as 0.5 s in the solution, and the simulated temperature increase was smooth and well agreed with the experimental results. A direct solver called Multifrontal Massively Parallel Sparse Direct Solver (MUMPS) with a tolerance of 10^{-5} was adopted to numerically solve the matrices assemble according to the governing equations and boundary conditions described above. The initial and boundary conditions were originated from the experimental measurements (such as the temperatures of inside air and the ambient). With Mie scattering, RTE, transient heat transfer equations coupled with varying boundary conditions, it is very demanding on the computational power. The Advanced Research Computing (ARC) at the University of Leeds was used to solve these equations in parallel.

5. Numerical results and analysis

5.1 Validation against experimental data

The absorption coefficients for gold nanoparticles and base fluid (water) calculated by Mie scattering theory (Eqs.3-5) are shown in **Fig. 6a**, where the volume concentration of gold nanoparticles is 5.8 ppm. The absorption coefficient is a key parameter for 3-D heat transfer and radiative transfer equations. As shown in **Fig. 6a**, gold nanoparticles mainly contribute to the absorption in the visible light range, and the base fluid (water) is more effective in the infrared range. To examine the reliability of our calculation, the absorbance from the numerical results based on Eq.10 is also compared with experimental data in **Fig. 6b**. The simulation result is generally in good agreement with the experimental data (i.e., maximum deviation within 8.5%). The relatively large deviation in the wavelength of 600~800 nm is due to the existence of some bigger particles in the nanofluids, leading to a red shift for the absorbance.

Under the same initial and boundary conditions, a comparison between the simulation and experimental results under constant solar intensity (i.e., 950 W/m^2) is shown in **Fig. 7**. The temperature rise for 1.45 ppm gold nanofluid is much higher than that of DI water, for instance $\sim 25^\circ\text{C}$ for nanofluid and $\sim 12^\circ\text{C}$ for DI water. However, both nanofluid and water exhibit obviously non-uniform temperature distribution during the

illumination, as much as $4.4\text{ }^{\circ}\text{C}$ and $1.9\text{ }^{\circ}\text{C}$ temperature differences, respectively. The high temperature at the top layer (TC1) shows that solar energy is mostly absorbed in the surface layer. The low temperature at the bottom layer is related to the effects of solar intensity decay along the optical path and limited heat conduction capability of the fluid. After about three hours' illumination, the gold nanofluid can reach a steady state temperature of $\sim 57\text{ }^{\circ}\text{C}$, but for water, it is only $\sim 45\text{ }^{\circ}\text{C}$, indicating that gold nanofluid even with a very low concentration can significantly enhance the solar photothermal conversion.

5.2 Temperature distribution inside the tube

Non-uniform temperature distribution is demonstrated through T -profile in the 3-D nanofluid (gold nanofluid with a volume concentration of 1.45 ppm, water as the based fluid, under constant solar intensity of 950 W/m^2), which is shown in **Fig. 8a**. The simulation result shows that the temperature at the top half of the tube along the Y direction is obviously higher than the bulk value. Generally, the highest temperature is located inside the nanofluid volume (about 0.8 cm from the top surface), for example $44\text{ }^{\circ}\text{C}$ in this case. Clearly larger temperature difference (i.e., more than $6\text{ }^{\circ}\text{C}$) for the whole volume is shown in **Fig. 8b**, comparing with the 3 thermocouple measurements in **Fig. 7**, which indicates the danger of using only one thermocouple to calculate the PTE, because it may lead to significant inaccuracy.

5.3 Efficiency prediction and comparison

Most previous studies such as Lenert et al. (Lenert and Wang, 2012) were based on experimental or simulated temperature field to optimize the efficiency of nanofluid-based DASC. Here we report a mathematical method to predict the absorption efficiency (ABE), which is based on the radiative transfer equations, as shown in Eqs. (10) and (11). In fact, thermal energy converted from solar radiative form should include three parts: sensible heat (i.e. bulk temperature increase), latent heat (i.e. due to fluid evaporation) and heat loss due to radiation and convection. As discussed earlier, PTE was obtained from experimental results that consider only the sensible heat contribution, which would underestimate the PTE. The proposed ABE can

be obtained from the optical properties of nanofluids and represents the maximum possible efficiency for any nanofluid-based solar system.

Fig. 9a shows the spectral absorption efficiency in different wavelength at a typical optical depth of 0.03 m. Clearly comparing to the water case, much higher ABE is observed for gold nanofluids across the whole solar spectrum. The spectrum ABE increases with the particle concentration, and nearly 100% ABE is achieved for 5.8 ppm nanofluids in the visible light spectrum, which is related to the Surface Plasmon Resonance phenomenon of gold nanoparticles. The small depression at ~900 nm is associated with the poor absorption performance in the near-infrared, which can be explained by the Mie scattering theory.

Fig. 9b and **c** show the ABE as a function of optical length L and particle concentration f_v . At the beginning, the efficiency of the nanofluids receiver increases rapidly with L , then asymptotically reaches 100%. This result is similar to Zhang et al.'s experimental observation(Zhang et al., 2014), where it showed clearly that the PTE increased nonlinearly with the volume concentration but no proper explanation was provided. As shown in radiative transfer equations (Eq. 9), the radiative transport energy is consumed inside the nanofluid exponentially, and the PTE should exhibit a nonlinear dependence on the particle concentration.

Fig. 9 also reveals the important parameters that determine the maximum possible solar receiver efficiency. The impact of the optical depth L and particle concentration f_v is embedded in the exponential term as $L \cdot f_v$ in Eq. 9. **Fig. 9b** reveals that both particle concentration and optical depth should be in relatively small values to achieve an optimized effect, as higher volume concentration of nanoparticle (i.e., more than 10 ppm for $L=0.05$ m) increases the efficiency slightly. Comparing to nanofluids, the efficiency depends more on the optical depth to reach a relative high value (i.e., 25 m for 80%). Overall, employing GNPs enhances the ABE significantly compared with DI water.

In order to compare the prediction of ABE against experimental data (i.e., where the optical depth is not a constant), a modified equation is proposed by integrating the efficiency with the radius of cylinder solar

419 receiver, as:

$$420 \quad \eta(f_v) = \frac{\int_0^R \int_{0.2\mu\text{m}}^{3\mu\text{m}} E_0(\lambda) (1 - e^{-2\kappa(\lambda, f_v)r}) d\lambda dr}{R \int_{0.2\mu\text{m}}^{3\mu\text{m}} E_0(\lambda) d\lambda} \quad (11)$$

421 where R is the radius of cylindrical tube. The ABE becomes an only function of volume concentration. The
 422 ABE is compared in three ways with photothermal conversion efficiency calculation based on temperature
 423 field, i) from one point temperature measurement, ii) from the average temperature measured by three
 424 thermocouples, and iii) from the simulated temperature field. For the simulated data, the efficiency is obtained
 425 by considering temperature difference in each computational nodes, as:

$$426 \quad \eta = \frac{\sum_{i=1}^n c_w \rho_w V_i \Delta T_i}{IA \Delta t} \quad (12)$$

427 **Fig. 10a** shows reasonably good agreement from four different methods (i.e., similar trend and maximum
 428 deviation within 7%). It can be expected that ABE from Eq. 12 is the theoretically maximum efficiency, in
 429 which the scattering and heat leakage are not considered. It can be used as an efficient method for nanoparticle
 430 selection and solar collector optimization without the need of measuring or calculating the temperature field.
 431 Photothermal efficiency based on only one temperature point shows a large deviation of the PTE for all
 432 samples. What's more, the situation becomes worse when the concentration of nanofluids increases, as shown
 433 in **Fig. 10a**. For example, the lowest PTE based on one temperature point is 12% lower than that from the
 434 experimentally determined average temperature at $f_v=5.8$ ppm.

435 What's more, the temperature used to determine PTE is usually at the beginning when the heat leak is not
 436 significant, the temperature difference (i.e., 4.4°C for 1.45 ppm under 950 W/m^2 solar intensity) inside the
 437 nanofluid is comparable to this temperature range ($10\text{-}15^\circ\text{C}$). Neglecting the non-uniform temperature
 438 distribution could cause significant inaccuracy (with an uncertainty of 29%-44%) in calculating the energy
 439 efficiency. To illustrate such an effect, **Fig. 10b** shows the maximum differences in temperature and PTE based

on the simulation results under a solar intensity of 950 W/m^2 and particle size of 20 nm. Here the temperature elevation employed to determine PTE is 10°C from the beginning of the experiment. Depending on the measurement locations, as high as 67% uncertainty could be obtained for the case of 5.8 ppm gold nanofluid.

The temperature non-uniformity issue will become more serious when the volume concentration of the nanofluids or the radiation intensity increases (i.e., under focused solar radiation). Quite a few recent studies (Hogan et al., 2014; Neumann et al., 2013a, 2013b; Ni et al., 2015) have shown that under a focused sunlight, i.e., via a typical Fresnel lens, rapid steam can be produced from plasmonic nanofluids albeit the bulk solution was still under the subcooled conditions. In one study (Neumann et al., 2013b), by using very dilute gold nanoparticles (16.7 ppm) under a solar concentration of 1000 Suns, steam generation efficiency was calculated as high as 80%, and only 20% of the absorbed solar energy was used to increase the bulk fluid temperature. However, there is still a strong debate if the steam can be produced directly around the heated nanoparticles. Considering the potential large temperature difference in the fluids under a focused solar intensity, there is a possibility that steam could be produced on the strongly heated surface layer, where strong evaporation or even boiling may occur. Further exploration of this issue is ongoing, and will be presented later.

6 Conclusions

Both outdoor experiments and simulation study were conducted in this work to analyze the photothermal conversion characteristics of gold nanofluids, and a new method was proposed to predict the maximum efficiency based on only the optical properties of the nanofluids. The main conclusions can be summarized as:

(1) The photothermal conversion efficiency (PTE) of gold nanofluids was much higher than that of DI water, which increased non-linearly with the nanoparticle concentration, reaching up to 76.0% at a concentration of 5.8 ppm.

(2) Significant non-uniform temperature distribution was observed inside the fluid, indicating that the consideration of average temperature is really needed to obtain a reliable PTE.

(3) A new method was developed to predict the radiative absorption efficiency based on only the optical properties of the nanofluid, without knowing the temperature field inside the fluid. This method can be used to identify the performance of different nanoparticles and optimize the solar absorbers efficiently.

(4) A radiative heat transfer model coupled with the Mie scattering theory was established. This model can predict the temperature profile inside the fluid, which confirmed the existence of large temperature difference inside the nanofluids.

(5) The comparison of various efficiencies shows that Eq. (11) can be used to predict the theoretically maximum photothermal conversion efficiency, and using only one-point temperature measurement could cause significant inaccuracy, i.e., an uncertainty up to 67.0% for 12.75 ppm gold nanofluid at 950 W/m^2 solar radiation.

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594

596 **Table captions:**

597 Table 1 Different cases of gold nanoparticles dispersions

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Figure captions:

Fig. 1. Nanoparticle characterization: (a) TEM image of gold nanoparticles (CASE 6); (b) **A**: absorbance of gold nanoparticle dispersions under different volume fraction; **B**: peak absorbance variation with concentrations in volume.

Fig. 2. Experimental setup: (a) Soar thermal illumination experiment under nature sunlight conditions (located on the roof of Human Machine and Environment Engineering Building in Beihang University in Beijing, 39° 59' 5.49" North, 116° 21' 18.70" East.); (c) A schematic illustration of experimental setup.

Fig. 3. (a) Temperature profile of differently diluted nanofluids under varied solar intensity (cloudy, solar intensity from about 400 W/m² to 700 W/m²); (b) Experimentally obtained increasing temperature profile of TC1-TC3 located inside the tube, concentration of nanofluids is 5.8 ppm and solar intensity is varied. (c) Comparison of three thermocouple signals for 0.72 ppm gold nanofluid under different solar intensities: constant solar intensity (i.e., about 950 W/m²) and varied solar intensity (i.e., from 400 W/m² to 700 W/m²).

Fig. 4. Variation of photothermal conversion efficiency (η) and specific absorption rate (SAR) with volume concentration for gold nanofluids under different solar intensities.

Fig. 5. (a) ASTM G173-03 Reference Spectra from literature, inset shows the solar energy distribution along with wavelength in percentage (integrating spectral emissive power with wavelength divided by irradiation intensity). (b) Calculation of spectral emissive power for sun ($T=5762$ K) and nanofluid ($T=303$ K), where spectral distribution is separated into two bands, A ($\lambda < 3000$ nm) and B ($\lambda > 3000$ nm).

Fig. 6. (a) Real and imaginary parts of m (Eq. (2)) and calculated absorption coefficients for gold nanoparticles (K_p), working fluid (K_f) and total (K) according to Mie scattering theory; (b) Absorbance from Eq. (10) in comparison with results from spectrophotometer.

Fig. 7. Experimentally obtained increasing temperature profile of TC1-TC3 located inside the tube, compared with numerical results from 3D model concentration of nanofluids is 1.45 ppm and solar intensity is constantly about 950 W/m².

Fig. 8. (a) Schematic for numerical simulation of a 3-D volumetric solar receiver based on gold nanofluid of concentration 1.45

ppm with normal nature solar radiation $I=900 \text{ W/m}^2$, where the geometry parameters can be seen in (b), solar radiation is in -y direction; (b) Temperature profiles in cross-section for nanofluid after 30 minutes' illumination (Global Tilt) at $x=0 \text{ cm}$.

Fig. 9. (a) Spectral efficiency which is defined as below in this paper:

$$\eta_{\lambda}(\lambda_c) = \left[\int_{0.2\mu\text{m}}^{\lambda_c} E_0(\lambda) (1 - e^{-\kappa(\lambda)L}) d\lambda \right] / \left[\int_{0.2\mu\text{m}}^{\lambda_c} E_0(\lambda) d\lambda \right], \text{ where a typical optical depth } L=0.03 \text{ m was chosen; (b) Absorption}$$

efficiency (ABE) as a function of optical length L for 5 different volume concentrations (inset: DI water); (c) ABE as a function of volume concentration f_v for 5 different optical lengths.

Fig. 10. (a) Comparison of the experimentally obtained photothermal conversion efficiency based on average temperature, efficiency calculated from 3D model and predicted absorption efficiency, area filled with color indicates the calculated efficiency range based on only one thermocouple; (b) Maximum efficiency uncertainty caused by non-uniform temperature distribution in the nanofluids

Table 1 Different cases of gold nanoparticles dispersions

Case No.	Reagents	Reaction time	Color	Peak size
1	HAuCl ₄ : 100ml 2.4×10 ⁻⁶ mol/L Sodium Citrate: 10ml 0.034mol/L	30 min	Wine red	9nm
2	HAuCl ₄ : 100ml 2.4×10 ⁻⁶ mol/L Sodium Citrate: 5ml 0.034mol/L	30 min	Orange	15nm
3	HAuCl ₄ : 100ml 2.4×10 ⁻⁶ mol/L Sodium Citrate: 2ml 0.034mol/L	40 min	Pink	25nm
4	HAuCl ₄ : 100ml 2.4×10 ⁻⁶ mol/L Sodium Citrate: 0.7ml 0.034mol/L	60 min	Crystal violet	65nm
5	HAuCl ₄ : 100ml 2.4×10 ⁻⁶ mol/L Sodium Citrate: 0.3ml 0.034mol/L	90 min	Ash black	120nm
6	HAuCl ₄ : 50ml 5×10 ⁻⁶ mol/L Sodium Citrate: 50ml 1×10 ⁻⁵ mol/L	20 min	Red purple	19nm

635

(a)

636

(b)

637

638

Fig. 1. Nanoparticle characterization: (a) TEM image of gold nanoparticles (CASE 6); (b) **A**: spectrum-dependent absorbance of

639

gold nanofluid under different volume concentrations; **B**: peak absorbance variation with nanoparticle concentrations

(a)

640

(b)

1. Thermocouples
2. Nanofluid
3. Air
4. Data acquisition
5. PC
6. Vacuum interlayer
7. Solar radiative intensity sensor

641

642 **Fig. 2.** Experimental setup: (a) Soar thermal illumination experiment under natural sunlight conditions (location: 39° 59' 5.49"

643 North, 116° 21' 18.70" East.) and (b) A schematic view of the experimental setup

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Fig. 3. (a) Example temperature profile of different nanofluids under a cloudy day (solar intensity varied from about 400 W/m² to 700 W/m²); (b) Temperature profile of TC1-TC3 located inside the fluid for 5.8 ppm nanofluid and DI water in the cloudy day. (c) Comparison of three thermocouple profiles for 0.72 ppm gold nanofluid under different solar intensities: constant solar intensity (i.e., about 950 W/m²) and varied solar intensity (i.e., from 400 W/m² to 700 W/m²)

Fig. 4. Variation of photothermal conversion efficiency (η) and specific absorption rate (SAR) with volume concentration of

653 gold nanofluids under different solar intensities

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658 **Fig. 5.** (a) ASTM G173-03 Reference Spectra from literature, inset shows the solar energy distribution with wavelength in
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660 emissive power for sun ($T=5762$ K) and nanofluid ($T=303$ K), where spectral distribution is separated into two bands, **A**
661 ($\lambda < 3000$ nm) and **B** ($\lambda > 3000$ nm)

Fig.6. (a) Real and imaginary parts of m (Eq. (2)) and calculated absorption coefficients for gold nanoparticles (κ_p), working fluid (κ_f) and total (κ) according to Mie scattering theory; (b) Absorbance from Eq. (10) in comparison to the results from the UV-Vis spectrophotometer

Fig. 7. Comparison between experimentally obtained temperature profile of TC1-TC3 with numerical results from 3D model (nanofluids concentration is 1.45 ppm and solar intensity is constantly at $\sim 950 \text{ W/m}^2$)

(a)

Fig. 8. (a) Schematic illustration of numerical simulation of a 3-D volumetric solar receiver where the geometry parameters are shown in (b) and solar radiation is in -y direction; (b) Temperature contour and cross-sectional profiles for nanofluid after 30 minutes' illumination (Global tilt, $x=0$ cm, gold nanofluid concentration = 1.45 ppm, and solar intensity $I=950$ W/m²)

(b)

(c)

Fig. 9. (a) Spectral absorption efficiency at different wavelengths in this paper:

$\eta_{\lambda}(\lambda_c) = \left[\int_{0.2\mu m}^{\lambda_c} E_0(\lambda) (1 - e^{-\kappa(\lambda)L}) d\lambda \right] / \left[\int_{0.2\mu m}^{\lambda_c} E_0(\lambda) d\lambda \right]$, where a typical optical depth $L=0.03$ m was chosen; (b) Absorption

efficiency (ABE) as a function of optical length L for five different volume concentrations (inset: DI water); (c) ABE as a

function of volume concentration f_v for five different optical lengths

Fig. 10. (a) Comparison of the experimentally obtained photothermal conversion efficiency based on average temperature, efficiency calculated from 3D model and predicted absorption efficiency, area filled with color indicates the calculated efficiency range based on only one thermocouple; (b) The maximum efficiency uncertainty caused by non-uniform temperature distribution in the nanofluids