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Chapter

Solar Thermal Conversion of Plasmonic Nanofluids: Fundamentals and Applications

Meijie Chen, Xingyu Chen and Dongling Wu

Abstract

Plasmonic nanofluids show great interests for light-matter applications due to the tunable optical properties. By tuning the nanoparticle (NP) parameters (material, shape, and size) or base fluid, plasmonic nanofluids can either absorb or transmit the specific solar spectrum and thus making nanofluids ideal candidates for various solar applications, such as: full spectrum absorption in direct solar absorption collectors, selective absorption or transmittance in solar photovoltaic/thermal (PV/T) systems, and local heating in the solar evaporation or nanobubble generation. In this chapter, we first summarized the preparation methods of plasmonic nanofluids, including the NP preparation based on the top-down and bottom-up, and the nanofluid preparation based on one-step and two-step. And then solar absorption performance of plasmonic nanofluids based on the theoretical and experimental design were discussed to broaden the absorption spectrum of plasmonic nanofluids. At last, solar thermal applications and challenges, including the applications of direct solar absorption collectors, solar PT/V systems, solar distillation, were introduced to promote the development of plasmon nanofluids.

Keywords: solar thermal, plasmonic, nanofluid, absorption, nanoparticle

1. Introduction

Nowadays, with the development of society and the improvement of people's living standards, environment issues, such as: greenhouse effect, acid rain, and haze, has become more serious. Developing green energy technology has attracted more researchers' attention, especially for solar energy, which is universal, harmless, huge, and sustainable. Solar utilizations can be divided into two main categories: solar-electric and solar-thermal. And both of them are needed to enhance the solar absorption performance of working media at its first step of solar conversion applications.

Solar thermal conversion is one of the most simple and direct ways of solar utilizations by heating the working mediums directly for follow-up usages, which can be widely used in the solar thermal collectors [1], solar distillation [2, 3] and so on [4]. Therefore, it's critical to improve the solar absorption performance of working mediums for the solar thermal conversion applications. For example, based on the surface absorber, various nanostructure coatings (e.g., grating, porous structure, and so on [5, 6]) were designed to achieve the selective absorption ability,

which serves as solar selective absorbers by heating the surface and transferring the heat to the working fluid for the follow-up applications. The heat loss from the absorbed surface due to the high temperature and heat transferred resistance between the absorbed surface and working should be considered during the design processes, which also limits its large-scale practical application at the high or middle temperature solar thermal conversion applications.

Instead of absorbing solar energy by a surface, work fluid can be used to absorb solar energy, which serves as both the solar absorber and heat transfer medium and can avoid the local high temperature area and reduce the heat transfer resistance. However, the common working fluids such as: water, oil, and alcohol usually have the limited solar absorption ability [7]. It was found that adding nanoparticles (NPs) to these working fluid (i.e., nanofluid) can greatly improve the solar collector efficiency [8, 9]. Nanofluid is a suspension of NPs (1–100 nm) in a conventional base fluid, which was first used by Choi in 1995 [10]. Nanofluids show unique characteristics in many aspects, including the heat transfer [11, 12] and the solar absorption ability due to the interaction between the light and NPs at nanoscale [9, 13]. For example, carbon nanotube, graphite and the other black carbon NPs were added into the base fluid to achieve the great solar absorption performance [14].

Plasmonic nanofluids show great interests to improve the absorption ability by dispersing plasmonic NPs in the base fluid stability. Due to the surface plasmon resonance (SPR) around the NP surface [15], the incident electric coupled with the free electron oscillation around the NP surface at the resonance frequency can strongly enhance the absorption performance of NPs [16] in **Figure 1**. The optical absorption performance of nanofluids can be enhanced by tuning the NP shape, size, or base fluid. Using plasmonic nanofluids as the absorber and heat transfer medium in the solar thermal applications shows great potential due to the excellent optical and thermal characteristics. To choose a proper nanofluids for specific solar thermal applications (such as: solar collectors, solar PV/T systems), many researchers investigated the optical and thermal properties of various nanofluids. For example, for the direct absorption solar collectors (DASCs), nanofluids as the absorber need to absorb the solar radiation in the full solar spectrum (0.3–2.5 um). While the nanofluid only serves as a beam splitter (i.e., selective absorber) in solar PV/T systems, which absorbs the useless spectrum for the PV cell and avoids heating the PV cells to improve the overall PV/T efficiency [4]. Hence, the optical absorption performance of plasmonic nanofluids should be considered in different solar thermal applications.

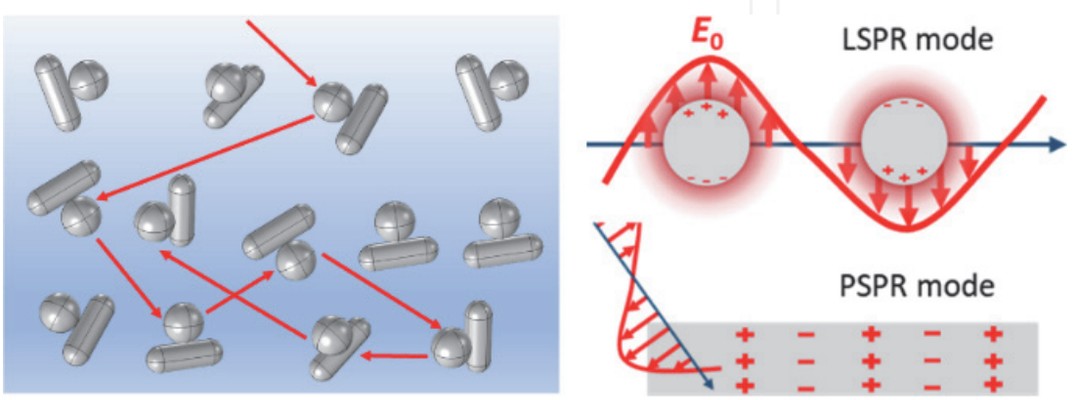

Figure 1.
Light propagation in the nanofluid [17] and the surface plasmon resonance (SPR) around the NP surface, dividing into localized and propagating surface plasmon resonance (LSPR and PSPR).

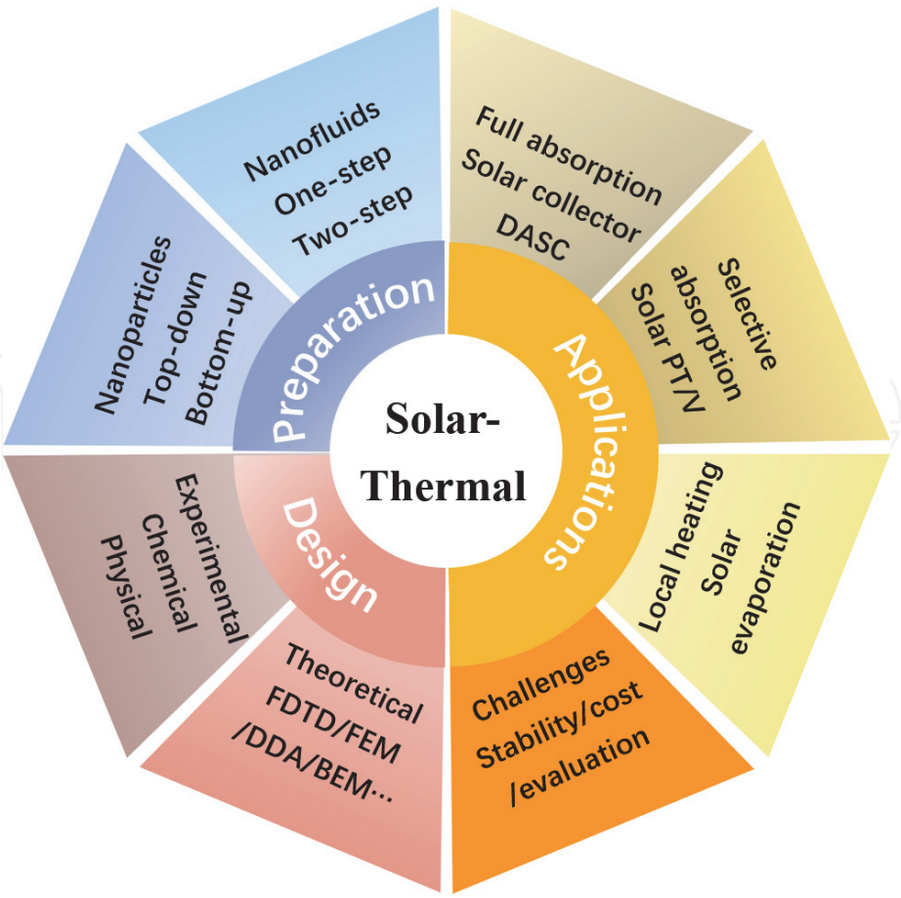

Figure 2.
The main parts of this chapter for solar thermal conversion of plasmonic nanofluids.

In this chapter, we focus on the solar thermal conversion of plasmonic nanofluids in **Figure 2**, which consists of the following three parts: 1) plasmonic nanofluid preparation including NPs and nanofluids; 2) solar absorption of plasmonic nanofluids based on the theoretical and experimental design; 3) solar thermal applications and challenges, including direct solar absorption collectors, solar PT/V systems, solar evaporation, other applications and challenges. To increase the understanding of previous studies, related analyses and calculation techniques are illustrated. This chapter is expected to provide researchers with deep insight into the solar thermal conversion of plasmonic nanofluids and facilitate future studies in this field.

2. Plasmonic nanofluid preparation

As discussed above, the NP parameters and dispersed base fluid have great effect on the optical absorption and solar thermal conversion performance of plasmonic nanofluids. We will first discuss the preparation methods of plasmonic nanofluids, and then the preparation methods of plasmonic NPs (**Figure 3**) are summarized due to the great interaction of NP parameters with the light. In this section, some common methods to prepare plasmonic NPs or nanofluids are listed and their advantages or limitation would also be discussed.

2.1 Plasmonic nanofluid preparation

The preparation method of nanofluids can be classified into two main categories in **Figure 3a**: one-step method and two-step method [18].

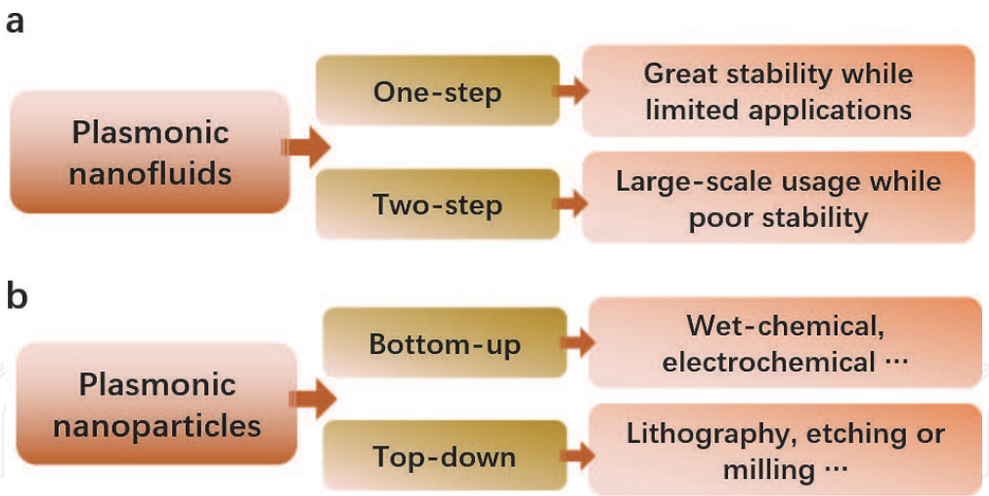

Figure 3.
Preparation methods of (a) plasmonic nanofluids and (b) nanoparticles.

The one-step method is to disperse NPs in the NP synthesis process by using the physical method or wet-chemical method. The prepared nanofluid is relatively stable by avoiding the NP separation process (e.g., centrifuge or drying) and redisperse process (e.g., stirring or ultrasonic oscillation). Hence, the one-step method can reduce NP agglomeration or sedimentation in the nanofluids. For example, an ultrasound-assisted one-step method was used to prepare spherical and plate-shaped Au NPs with the NP size of 10 ~ 300 nm [19]. But the dispersed base fluid has limitations, which usually consists of the residual chemical reagent in the NP synthesize process and the nanofluid could not be applied in a large-scale range.

The two-step method separates the NP synthesis process from the dispersion process, which is widely used in the large-scale applications. In this method, various NPs, such as: nanospheres, nanorods, nanotubes, and so on, are in the state of dry powders and then these NPs can be dispersed into different base fluids by stirring or ultrasonic oscillation for different applications. Due to the redispersion process of NPs, the stability is worse than that of the one-step method, but the two-step method has a simple preparation process, a high NP controllability, and wide application ranges. It can be seen from the two-step method that the NP parameters, such as the size, morphology, and dielectric environment of the base fluid determine their unique SPRs. Therefore, for solar thermal conversion applications of plasmonic nanofluids, preparing plasmonic NPs with the controllable morphology and size is the prerequisite and basis for their applications. And the fabrication of these plasmonic NPs will be discussed in the next section.

2.2 Plasmonic nanoparticle fabrication

The fraction processes of plasmonic NPs can be divided into two main categories in **Figure 3b**: the top-down based on the lithography, etching or milling, and the bottom-up, including the seed-mediated growth, chemical reduction, electrochemical method, and so on. Given that the NP shape can significantly affect the way it interacts with light and its SPRs, researchers have made great efforts to develop preparation methods for plasmonic NPs with the reproducible control of the size and shape. Nowadays, it's possible to fabricate high-quality plasmonic NPs (e.g., Au or Ag) with the target SPR wavelengths or near-field enhancement by enabling a systematic study of SPR dependencies on the size, shape, and structure of plasmonic NPs.

The wet-chemical method is one of the most common bottom-up methods to tune the size or shape of metal NPs. For Au NPs, chloroauric acid ($HAuCl_4$) in aqueous solution is usually used as the precursor and the reducing agent can be polyvinyl pyrrolidone (PVP), Sodium borohydride ($NaBH_4$), ascorbic acid (AA), sodium citrate (SC), and so on. The reduction reaction is also determined by the temperature. And various Au NP shapes can be achieved by introducing the additive, e.g., etyltrimethylammonium bromide (CTAB) for nanorods [20], sodium citrate or trisodium citrate for spheres [21], silver iron (Ag^+) for thorns [22]. Au NPs with the size ranged from 5 nm to 150 nm can be obtained by changing the concentration of the precursor and the reducing agent [23], PH value [24], temperature [25] and so on [26]. Seed-medicated method is another effective method to control the size and shape of Au NPs, which divides the reaction into nucleation and growth stages separately, so that the size and morphology of the particles can be controlled in a larger range [27]. By controlling the growth rate of different crystal planes, the final synthesized NPs can deviate from the initial seed crystal structure by the seed growth method. For example, cube Au NPs were prepared by the amount of ascorbic acid (AA) in the growth solution and the size can be controlled by the amount of seed solution or the growth number [28, 29]. Ag NPs also can be prepared by the similar methods using $AgNO_3$ or other silver salts. To scalable and green prepare metal NPs, a rotating electrodeposition and separation (REDS) technique developed, which entails electrochemically depositing NPs onto a continuously rotating metal foil and subsequently harvesting them through mechanical delamination. A wide array of elemental nanoparticles (e.g., Ag, Au, Ni, Cu), alloys nanoparticles (e.g., FeCoNi and FeCoNiW), and metal oxide nanomaterials (e.g., CO_3O_4) were synthesized by REDS [30].

Besides the bottom-up method, top-down method is another to prepare NPs, which mainly including some physical method, such as: electron beam lithography (EBL), milling, annealing, laser-melting, and so on. The fabrication process of EBL is similar to classical photolithography, an electron beam is used to mark the pattern in the resist instead of light. [31]. Despite the low fabrication throughput and the fact that very small structures may be at the physical limit in terms of electronic function, the technique can find applications in preparation of reproducible large-scale arrays of plasmonic NP with arbitrary two-dimensional shapes. Among the disadvantages are the technological requirements such as high vacuum and a scanning electron microscope system, much longer time to write a pattern than photolithography. Using conventional lithography techniques many shapes of nanoparticles on surfaces can be achieved. However, large scale fabrication using reproducible patterns, inverse replication or transfer of NPs between substrates, and three-dimensional nanostructures including deep etching has been increasingly demanded in plasmonic nanostructures [32, 33].

After obtaining different plasmonic NPs, it should be dispersed into the working fluid stability to form various nanofluids. The fabrication of NPs based on the top-down method is expensive and consumed on the materials, which could not meet the scale requirement although the high-quality NPs can be achieved. Wet-chemical method can be an efficient method to achieve plasmonic NPs in the solar thermal conversion applications.

2.3 Nanofluid stability

Nanofluid is defined as dispersing NPs stability into the base fluid, which is not simply mixing solid NP phase and liquid phase. It's a complex colloid by dispersing specific functional NPs in the base fluid (e.g., water, oil and so on). The main challenge for nanofluid applications is how to produce well-dispersion nanofluids.

Owing to the interaction among different NPs at the nanoscale and gravity at Earth, NPs are usually agglomerated due to Van der Waals force and then trend to be sediment at the bottom [34]. As a result, the agglomeration and sedimentation of NPs in the base fluid would affect the optical absorption and heat transfer performance, weakening the system efficiency. In addition, recent studies showed that the agglomeration or sedimentation can be worse under harsh operating conditions, such as: high temperature and pressure [35, 36]. Many methods were used to evaluate the stability of nanofluids, the simplest and direct method is the sedimentation method [18]. Interface electromotive force analysis is another common method to observe the stability of nanofluids, but this method is limited by the viscosity and concentration of the fluid [37]. Wang et al. [38] used an ultraviolet–visible spectrophotometer to study the stability of nanofluids. The NP concentration can be obtained by measuring the change in the light absorption rate of the system with the sedimentation time because the NP concentration is a linear relationship with the absorbance of nanofluid at the low concentration.

The stability of plasmonic nanofluids is also one of the major issues limiting the applications of nanofluids. Many researchers have made much efforts to improve the stability of the plasmonic nanofluids from the aspect of long-time and high-temperature dispersion [39]. For example, Au@SiO_2 and Ag@SiO_2 core-shell NPs were synthesized using a low-temperature two-step solution process. Results showed that the synthesized metal@SiO_2 nanofluids exhibited excellent dispersion stability of 93.7% for Au@SiO_2 and 100% for Ag@SiO_2 in 6 months without using any surfactants, and they also showed a good thermal stability after thermal exposure at 150° C for an hour [40]. An ultrastable nanofluids with the broadband photothermal absorption was achieved using citrate and polyethylene glycol-coated Au NPs, circumventing the need for free surfactants. Electrostatic stabilization provided superior colloidal stability and more consistent optical properties; chemical and colloidal stability was verified for 16 months, the longest demonstration of stable nanofluids under ambient storage in the solar literature [41]. Besides the base fluid water used above, the base fluid oil was also studied to improve the stability. A facile and effective strategy, including controlled high-temperature synthesis of nanoparticles, surface modification of particles, and post-modification particle size partition, was designed to prepare stably dispersed silicone-oil-based nanofluids that enable high-temperature operation [42]. A low cost, and scalable method was reported to synthesize solar selective nanofluids from 'used engine oil' with the excellent long-term stability and photothermal conversion efficiency. Results showed that their stability and functional characteristics can retain even after extended periods (72hours) of high temperature (300 ° C) heating, ultra violet light exposure and thermal cyclic loading [43].

3. Solar absorption of plasmonic nanofluids

The excellent optical absorption performance of plasmonic NPs make it to be a great candidate in the solar thermal conversion applications, which is critical for the solar thermal conversion applications. And the optical properties of nanofluids can be controlled by the NP size, shape, concentration and base fluid. In this section, we will discuss the optical properties of NPs or nanofluids from two aspects: theoretical design and experimental design.

3.1 Theoretical design

To achieve the optical properties of nanofluids, including transmittance, reflectance, and absorptance, the optical performance of single NP is usually determined

firstly. And the dielectric function of materials are required for the optical simulation, which is taken from the experimental data of bulk materials (e.g., Johnson and Christy [44],) or a model approximating experimental results (e.g., Drude method). The Drude model is the simplest of all, but disregards radiation damping. Even today, mainly because of the simplicity, the Drude model is still used to describe the dielectric functions in many calculations. In some problems, the classical models of dielectric functions are unsatisfactory but, at the same time, full quantum theories involve a very complex treatment including non-local effects [45], polarizabilities including non-linear terms [46], electron densities calculation using mean-field theories [47] and temperature dependent effects [48]. The need for quantum treatment of the optical properties of small particles has been evidenced in recent experimental studies [49]. In large particles the resonances are influenced by retardation effects and are strongly dependent on the size of particles, but the dielectric function can be assumed as that of bulk. Based on the dielectric function, Au, Ag and Al are the three most used materials in plasmonics. Their SPR wavelengths are at visible or UV spectral bands and, therefore, of great potential in solar thermal applications.

Mie theory: Mie theory is a simple and theoretical method to calculate the optical properties of sphere NPs in a homogenous medium, which uses a series of coefficients a_n and b_n for the scattered fields and c_n and d_n for the internal fields to determine the scattering fields. The scattering and extinction cross sections can be calculated as: [50].

$$C_{scat} = \frac{2\pi}{k^2}\sum_{n=1}^{\infty}(2n+1)\left(|a_n|^2 + |b_n|^2\right) \tag{1}$$

$$C_{ext} = \frac{2\pi}{k^2}\sum_{n=1}^{\infty}(2n+1)\,\mathrm{Re}\,(a_n + b_n) \tag{2}$$

The absorption cross section can be obtained as: $C_{abs} = C_{ext} - C_{scat}$. Despite to the less computation load, it is possible to obtain cross-sections for many wavelengths in a few seconds, using a common PC. However, a large number of terms is required for accurate cross-section calculations of spheres with very large size parameter [51]. The Mie theory has been extended to permit calculations for ellipsoidal shape, multilayer or several spheres [52].

DDA: To calculate the light scattering of an arbitrary shape NP, discrete dipole approximation (DDA) was first presented by Purcell and Pennypacker [53] by using a grid of dipoles. To occupy by the scattering target, DDA method discretizes the volume by an array of N dipoles using Clausius–Mossotti polarizability α_j for each dipole, which interacts with the incident field and the neighbors. The polarization of dipole j located at r_j can be determined by $P_j = \alpha_j E_j$, and the field can be calculated as:

$$E_j = E_j^{inc} - \sum_{k\neq j} A_{jk} P_k \tag{3}$$

where $E_j^{inc} = E_0 e^{ikr - i\omega t}$. A_{jk} is the matric of dipole interaction and retardation effect.

To achieve accurate and reproduce the calculation results, two validity conditions should be verified in DDA: (a) the dipole lattice spacing d should be small enough, i.e., $|m|kd \leq 1$, where m is the complex refractive index of the scattering target. (b) d must be small enough to refabricate accurately the NP shape. For small plasmonic NPs, or small inter-particle separations, d must be smaller than 1 nm.

BEM: Boundary element method (BEM) is another method to calculate the optical properties of plasmonic nanostructures, which was introduced by García de Abajo and Howie [54] using the following equations:

$$\phi(r) = \phi_j^{ext}(r) + \int_{S_j} G_j(|r-s|)\sigma_j(s)ds \tag{4}$$

$$A(r) = A_j^{ext}(r) + \int_{S_j} G_j(|r-s|)h_j(s)ds \tag{5}$$

where $\phi(r)$ is the electric potential, $A(r)$ is the vector potential, $\sigma_j(r')$ is the surface charge density and $h_j(r')$ is the surface current density and G_j is the Green's function of Helmholtz equation inside each homogeneous medium of dielectric function. S_j is the boundary of the medium j. s is the point of the boundary between medias. r is the point inside the medium. $\phi^{ext}(r)$ and $A^{ext}(r)$ are the potentials at the interface caused by external sources and the full space is filled by a homogeneous medium j. Therefore, a much smaller number of elements is required to evaluate the fields than volume integral based methods, but involving a complex parameterization of the boundary elements.

FDTD: Finite-difference time-domain (FDTD) is one of the most popular optical calculation methods in plasmonic nanostructures, which is first developed by Yee in 1966 [55]. The basis of the model is from Maxwell equations in electrodynamics. The second-order precision central difference is used to approximate the discretization of the differential form of Maxwell equations, thereby a set of time-domain propulsion formulas can be used to deal with electromagnetic wave propagation problems. Since the FDTD method directly discretizes the time-domain wave equation, it will not limit its application range due to mathematical models, and can effectively simulate various complex structures.

The popularity of this method has strongly increased in the last two decades, mainly due to the simplicity of implementation, support of arbitrary NP shape, allowing to investigate linear and non-linear properties of NPs, using Maxwell's equations directly without approximations. There are, however, some undesired effects, like the staircase of fields in non-rectangular boundaries, mainly in code implementations without adaptive meshing. To avoid this, very fine discretization or sub-pixel smoothing of the dielectric function must be applied [56]. The dielectric function of the materials requires analytical expressions (e.g., Drude–Lorentz) [57].

FEM: Finite element method (FEM) was developed to solve differential equations of boundary-value problems [58]. Physical problems described by differential equations over a domain, like for example the Helmholtz equation in real three-dimensional space. Hence, electromagnetic (EM) field propagation around the single NP can be described by the Helmholtz Equation [59]:

$$\nabla \times \left(\mu_r^{-1}\nabla \times \boldsymbol{E}\right) - k_0^2\varepsilon_r\boldsymbol{E} = 0 \tag{6}$$

where $\boldsymbol{E}$ is the electric field of the medium, j is the current density, k_0 is the wavenumber, ε_r is the dielectric function, which is calculated as $\varepsilon_r = (n-ik)^2$, n and k are the complex refractive indices. Within each element $\boldsymbol{E}$ is approximated using a basis function expansion $\boldsymbol{E} = \sum_{j=1}^{n}\boldsymbol{N}_j\xi_j$, where the sum is over n interpolation point. $\boldsymbol{N}_j$ is chosen basis function and ξ_j is the unknown coefficient. A solution can be obtained by using the variational principle to determine ξ_j. To obtain a meaningful solution, $\boldsymbol{N}_j$ is required to satisfy Gauss's law and appropriate boundary conditions on the surface of all elements. During the last decade, an increasing

number of publications on plasmonic nanostructures done with COMSOL Multiphysics has appeared in the literature.

A short comparison of these above calculation methods for NPs are listed in **Table 1**. The choice of the calculation method depends on many factors, such as: NP size, shape and dielectric environment. But the general method, such as: FEM, and FDTD, can be used in most situations by applying the periodic boundary conditions at the sides of the unit cell.

The optical properties of nanofluids also can be calculated based on the above method, such as: FDTD or FEM, which are the direct way to achieve the absorption performance of nanofluids without the strict assumptions. But the computation load is large for nanofluids since the geometry size ($\sim$ mm) is much larger than NP size or mesh size ($\sim$ nm). Therefore, the optical properties of nanofluids can be obtained from the optical properties of single NP due to the low NP concentration of plasmonic nanofluids in the solar thermal conversion applications and the independent scattering can be applied in the calculation of nanofluids.

One method is to avoid the scattering effect of NPs due to the small size, resulting in the negligible scattering effect in the nanofluids. Therefore, the absorption efficiency of the nanofluids can be obtained by the independent scattering approximation, which can be described as [9]:

$$k_{a\lambda,nf} = k_{a\lambda,bf} + k_{a\lambda,np} = \frac{4\pi\kappa}{\lambda} + \frac{f_v C_{abs}}{V_{np}} \tag{7}$$

where $k_{a\lambda,nf}$, $k_{a\lambda,bf}$, and $k_{a\lambda,np}$ are the absorption coefficients of the nanofluid, the base fluid water and the NPs respectively. κ is the absorption index of water. f_v is the NP volume fraction. V_{np} is the single NP volume. C_{abs} is the absorption cross section of the NP. Based on the Beer–Lambert law [61], the radiation intensity decays exponentially along the transmission direction. Therefore, the solar absorption efficiency η_{abs} can be calculated as:

$$\eta_{abs} = \frac{\int_{0.3\mu m}^{2.5\mu m} I_{abs}(\lambda)d\lambda}{\int_{0.3\mu m}^{2.5\mu m} I_s(\lambda)d\lambda} = \frac{\int_{0.3\mu m}^{2.5\mu m} I_s(\lambda)\left(1 - e^{-Hk_{a\lambda,nf}}\right)d\lambda}{\int_{0.3\mu m}^{2.5\mu m} I_s(\lambda)d\lambda} \tag{8}$$

where $I_s(\lambda)$ is the solar spectra at AM 1.5. $I_{abs}(\lambda)$ is the absorbed spectra. H is the depth.

Method	Description	Advantages	Limitations
Mie theory	Theoretical result	Accurate solution	Valid for simple shapes (such as: sphere)
DDA	Approximate result based on discrete dipoles	Arbitrary shape	Time-consuming; large memory space for large NPs
BEM	Numeric solution with surface discretization	Fast calculation than volume methods	Complex parameterization of boundary elements
FEM	Differential equations solved over a domain	General application	Time-consuming; large memory space for complex structures
FDTD	Discretization of Maxwell equation with Yee cell	General application	Computational stability depends on dielectric functions; Time-consuming for spectral calculations

Table 1.
Comparison of calculation methods for plasmonic NPs [60].

The optical properties of nanofluids also can be solved by the Monte Carlo (MC) method to obtain the solar absorption performance of nanofluids. MC technique is a flexible method for simulating light propagation in the medium. The simulation is based on the random walks that photons make as they travel, which are chosen by statistically sampling the probability distributions for step size and angular deflection per scattering event. After propagating many photons, the net distribution of all the photon paths yields an accurate approximation to reality. In this method, the scattering effect is considered by the scattering efficiency and scattering phase function. The absorptance, transmittance, and reflectance of nanofluids can be calculated by counting the fate of photons.

For the plasmonic nanofluids applied in the solar thermal applications, the absorption spectral distribution is one of the most important parameters, which is proportional to the NP parameters (concentration, shape and size), Qin et al. theoretically optimized the spectral absorption coefficient of an ideal plasmonic nanofluid for a DASC to maximize the thermal efficiency while maintaining the magnitude of the average absorption coefficient at a certain value [62]. However, considering that the SPR frequency of metallic NPs, such as Au, Ag, and Al, is usually located in the ultraviolet to visible range. The actual plasmonic nanofluids usually have the narrow absorption band due to the SPRs. Two strategies can be adopted to overcome this shortage in the NP theoretical design process.

One is to blend NPs with different absorption peaks to form hybrid plasmonic nanofluids for full utilization of solar energy in a broad spectrum. For example, an ideal distribution of spherical metal NPs, including nanospheres and nanoshells, were designed to match the AM 1.5 solar spectrum with an determination of absorbing and scattering distributions [63]. Based on MC method and FEM, four type of Au nanoshells were blended in the base fluid to enhance the solar absorption performance of plasmonic nanofluids with an extremely low particle concentration (e.g., approximately 70% for a 0.05% particle volume fraction) [64]. By applying the customized genetic algorithm, an optimal combination for a blended nanofluid (metal nanosphere, metal@SiO_2 core-shell, and metal nanorod) was designed with the desired spectral distribution of the absorption coefficient [65]. Besides the core-shell NPs, other NP shapes were also designed to expand the absorbance over the entire solar spectrum [66, 67]. Although different blended NPs were designed to broad the absorption spectrum, the comparison or enhancement is usually done based on the single-element nanofluid, which is not enough to compare with the other blend styles.

The other is to design complex NP structures with multiple absorption peaks at different wavelengths or coupled with the great intrinsic absorption materials. For example, core-shell NPs (Al@CdS [68], Ag@SiO_2@CdS [69], Au@C [70], Ag@TiO_2 [71], and gallium-doped zinc oxide@Cu [72, 73]) were the direct way to enhance the solar absorption performance due to the enhancement and tunable SPRs of shell and intrinsic absorption of core by optical simulations, thus broadening the absorption spectrum and improving the solar absorption performance of plasmonic nanofluids. Results also found that Ag NPs with sharp edges can induce multiple absorption peaks due to both LSPR and lightning rod effect to broad the absorption spectrum [74]. In addition, a plasmonic dimer nanofluid, consisting of the rod and sphere, was proposed to enhance the solar absorption performance by LSPR, PSPR, and gap resonance between the rod and sphere at different wavelengths [17], which was also similar as the thorny NPs [75].

3.2 Experimental design

Although various NP structures were designed to enhance the solar absorption performance of plasmonic nanofluids theoretically, the synthesizes of these

complex structures are still difficult and more efforts still are needed to precious control the NP size parameters (e.g., size or shape) experimentally.

Compared with the other common nanofluids (e.g., SiO_2, TiO_2, Al), plasmonic Au nanofluids with the small NP size were prepared experimentally to obtain the great solar thermal conversion efficiency [21, 76]. However, the absorption peaks of these common metals usually locate in the visible part especially for the metal sphere. Multi-element NPs (such as: alloy NP [77]) can further enhance solar absorption ability compared with the single-element NPs by tuning the LSPR peak. Various core-shell NPs were also prepared to enhance the solar absorption performance of plasmonic nanofluids [73, 78]. For example: Ag@CdS core-shell NPs were synthesized by a facile method and the optical absorption performance of Ag@CdS nanofluids was enhanced in a wide range of visible light compared with bare Ag and CdS NPs [79]. Sn@SiO_2@Ag core-shell NPs were prepared with good abilities of both optical absorption and thermal energy storage [80]. Ag shell can improve light absorption due to LSPR effect, which was also can be found experimentally for CuO@Ag [81] and TiO_2@Ag plasmonic nanofluids compared with CuO, TiO_2, and Ag nanofluids [82].

Another simple way is to blend sphere NPs with different materials [83–85]. Various NPs have been blended experimentally to enhance the solar absorption performance of plasmonic nanofluids. For example, hybrid nanofluids containing reduced graphene oxides decorated with Ag NPs [86], multi-wall carbon nanotubes and SiO_2@Ag NPs [87], Fe_3O_4, Cu and Au NPs [88], and Au and TiN NPs [89] showed great solar absorption performance by tuning the ratios of different components to broaden the absorption spectrum. LSPR effect around plasmonic NPs and intrinsic absorption of semiconductor NPs make the hybrid nanofluids possess superior optical absorption to bare NPs at the same concentration. Besides the blended nanofluids with different NP materials discussed above, the other route is to blend the NPs with different shapes. For example, by mixing Au NPs (such as: nanorods [90]) with different shapes in water, a blended plasmonic nanofluid was prepared and absorption spectrum can be broadened due to the various LSPR peaks of different NP shapes [84]. The blended nanofluids based on Ag triangular nanosheets and Au nanorods, were proposed and a high efficiency of 76.9% is achieved experimentally with a very low volume concentration (0.0001%) [91].

As discussed above, blending different NPs is a simple way to achieve multi absorption peaks. However, compared with the single component NPs, the interaction between the different NPs in the blended nanofluids is limited due to independent scattering at the low NP fraction, leading that the solar thermal conversion efficiency of blended NPs was almost equal to the arithmetic sum of the efficiency of each component NPs without enhanced coupled effect between different NPs with the incident light [83]. Designing complex structures with multi-resonance peaks experimentally can be an efficient way to enhance the solar absorption performance of plasmonic nanofluids. For example, Au thorn [92] and Au dimer [93] were designed experimentally enhance the light absorption performance of plasmonic nanofluids. In addition, Janus NPs also showed great optical absorption performance due to the complex structure experimentally [94].

4. Applications

Nanofluids can either absorb or transmit specific solar spectrum and thus making assorted nanofluids ideal candidates for various solar applications [95]. Based on the tunable optical absorption performance of plasmonic nanofluids, several

applications, including full spectrum absorption in direct solar absorption collector, selective absorption in solar PT/V systems, and local heating in solar evaporation or steam generation, are discussed below in **Figure 4**.

Some efforts have been made to investigate the solar thermal conversion performance of stationary plasmonic nanofluids based on the direct solar absorption collectors (DASCs). A one-dimensional transient heat transfer analysis was carried out to analyze the effects of NP volume fraction, collector height, irradiation time, solar flux, and NP material on the collector efficiency. Results showed that the plasmonic nanofluids (e.g., Au and Ag) achieved the better collector efficiency in the stationary state [98]. Solar thermal conversion performance of Au nanofluids in a cylindrical tube under natural solar irradiation conditions was studied and a efficiency of 76.0% at a concentration of 5.8 ppm can be achieved [99]. Although Au nanofluids have high solar absorption performance, their expensive cost limits their practical use [100]. The solar thermal conversion performance of six (Ag, Cu Zn Fe, Si and Al_2O_3) common NPs in direct absorption solar collectors (DASC) was investigated under a focused simulated solar flux. Ag nanofluid turned out to be the best among all due its strong plasmonic resonance nature [101]. Stable silver nanofluids were prepared through a high-pressure homogenizer and the outdoor experiments were conducted under sunlight on a rooftop continuously for ~10 h and the excellent photothermal conversion capability even under very low concentrations can be achieved [102].

Recently, the direct-absorption parabolic-trough solar collector (DAPTSC) using the flow nanofluids has been proposed, and its thermal efficiency has been reported to be 5–10% higher than the conventional surface-based parabolic-trough solar collector. In order to reduce the cost of a collector and avoid NP agglomeration when using plasmonic nanofluids, the configuration with the lowest possible absorption coefficient but with the reasonably high temperature gain as well as efficiency was explored [103]. For the collector design, an extra glass tube inside was inserted so the nanofluid was separated into two concentric segmentations (i.e., an inner section and an outer section), and a nanofluid of lower concentration was applied in the outer section while a nanofluid of a higher concentration in the inner section. Results showed that at the same NP concentration parameter, the DAPTSCs with two concentric segmentations of nanofluids outperform those with one uniform nanofluid for all considered configurations [104]. Furthermore, the transparent DAPTSC was improved by applying a reflective coating on the upper half of the inner glass tube outer surface such that the optical path length was doubled compared to that of the transparent DAPTSC, allowing a reduction in the absorption coefficient of the nanofluid [105]. In addition, by replacing the semi-cylindrical reflective coating with a semi-cylindrical absorbing coating for exploiting both volumetric and surface absorption of the solar radiation. The DAPTSC with a

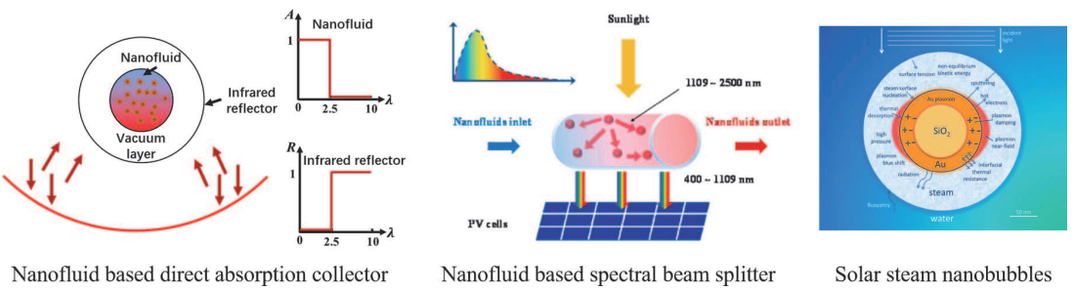

Figure 4.
Solar thermal applications of plasmonic nanofluids, including nanofluid based direct solar absorption collector, solar spectral beam splitter in solar PV/T systems [96], solar steam or nanobubble generation in solar evaporation [97].