Solar Spectral Beam Splitting Performance and Regulation Study on Aluminum-Based Nanofluid

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Abstract: This study aims to match the splitting characteristics of the nanofluid with the photovoltaic response and thus improve the efficiency of the concentrating photovoltaic thermal (CPV/T) system. In this paper, the optical properties of aluminum (Al) nanoparticles are investigated by using the finite-difference time-domain method, and it is found that changing the particle size can achieve the modulation of the extinction properties of nanoparticles, including the extinction intensity and resonance peak range. To optimize the optical properties of Al nanoparticles and to solve the problem of their easy oxidation, the extinction properties of Al@Ag nanoparticles with different shell thicknesses were designed and analyzed. It was found that the extinction ability of the particles with core-shell structure was enhanced. When Al and Al@Ag nanoparticles are dispersed into water to form nanofluid, the transmittance is effectively reduced in the short wavelength band compared to pure water. The core-shell structure can reduce the transmittance by up to 13% and 10% in the 350–650nm band compared with the pure Al particles of 50nm and 60nm particle size, and has almost no effect on the transmittance in the photovoltaic window (640–1080nm). Therefore, the efficiency of the CPV/T system can be effectively improved by the regulation of Al nanoparticles.

Keywords: Nanofluid; Photovoltaic/thermal; Spectral beam splitting; Finite-difference time-domain method

1. INTRODUCTION

In modern society, energy shortage and environmental pollution have prompted people to develop various renewable energy sources. Among them, solar energy, as a green energy source with wide distribution and huge reserves, is expected to replace fossil fuels to meet the energy demand of human beings and provide a reliable and sufficient energy supply [1,2]. However, due to the special spectral response characteristics of photovoltaic (PV) cells, only a portion of the solar radiation can be converted into electrical energy while the rest is dissipated in the form of heat [3], while the unwanted heat leads to overheating of PV cells, which further reduces their power generation efficiency [4]. In order to solve these problems, it has been proposed to introduce the spectral beam splitting (SBS) technique into the photovoltaic thermal (PV/T) system [5–8], which divides the solar radiation into two parts, one of which splits into the wavelength bands needed by the PV cell, while the remaining wavelength bands are converted into heat energy by the collector. The PV cell and collector are spatially separated from each other, avoiding the thermal coupling of the system, and the solar thermal and photovoltaic conversion can be carried out at different temperatures, which enables the PV cell to keep working efficiently while obtaining high-temperature thermal output, thus achieving the efficient utilization of the full spectrum of solar energy.

According to the principle of SBS, it can be divided into solid film interference beam splitter, liquid absorptive beam splitter, fluorescence beam splitter and holographic beam splitter, etc. [4,5,9], in which the liquid beam splitter can achieve the required wave band of photovoltaic cells with high transmittance and irradiate to the photovoltaic cell, and the rest of the wave band will be absorbed by beam splitter liquid and converted into heat directly, thus avoiding the heat loss caused by multiple heat exchange [10]. Liquid beam splitting technology is also divided into traditional and nanofluid splitting technology. Compared with the ordinary liquid beam splitter, nanofluid has adjustability, its optical properties are jointly determined by the base fluid and nanoparticles. In the case of the base fluid remains unchanged, the optical properties of the nanofluid can be regulated by changing the structure, size, type, or morphology of nanoparticles in order to meet the different application cases and different types of solar cells, and to avoid heat loss caused by multiple heat exchanges. Different electric-heat output ratios of concentrating photovoltaic thermal (CPV/T) systems can be achieved by regulating the nanofluid [11], which can meet different needs of life and production. However, there is still no beam splitting nanofluid that perfectly matches with photovoltaic cells until now.

In recent years, the unique localized surface plasmon resonances (LSPR) effect of metal nanoparticles has been generally emphasized in the field of near-field optics [12–15]. However, the absorption bandwidth of single-component LSPR nanoparticles tends to be limited to only a very narrow wavelength range, with low applicability and popularity to match the spectral frequency splitting requirements of specific applications [16,17]. Therefore, it is necessary to obtain nanoparticles with special structures through rational structural design to achieve continuous tunability of the optical properties of the particles. Most of the current studies are based on noble metal materials such as gold (Au) and silver (Ag), because Au and Ag have excellent extinction properties in the long wavelength band. However, the ideal photovoltaic band of photovoltaic cells in a SBS-CPV/T system also does not include the ultraviolet (UV) and near-UV bands, and the equipartition excitation resonance properties of the Au and Ag nanoparticles will not occur in the near-UV bands, hence the noble metal materials such as Au and Ag are not perfect nanomaterials.

Based on these problems, this paper selected aluminum (Al), which has excellent LSPR characteristics in the near-ultraviolet wavelength band, as the research object, and water, which can absorb incident energy at longer wavelengths, as the base fluid. The finite-difference time-domain method and the established optical transmittance model were used to simulate and analyze the effects of different particle sizes, core-shell structures, and optical path on the optical properties of Al nanoparticles and fluids, which provides theoretical guidance and optimization directions for finding nanofluids compatible with photovoltaic cells.

2. NUMERICAL SIMULATION

2.1. CALCULATION METHOD AND PHYSICAL MODEL

The finite-difference time-domain (FDTD) is a differential representation of Maxwell's system of equations that employs interleaved sampling in the space and time of the electric and magnetic field nodes, and it is used to solve problems related to the propagation of electromagnetic waves in a medium [18,19]. This method is now widely used in the nanophotonics community to effectively model the interaction of light with various materials and optical devices, and it can be used to study the optical properties of various materials such as reflectivity, transmittance, absorption, and interference. In this paper, the optical properties of Al nanoparticles have been studied by using FDTD Solutions software.

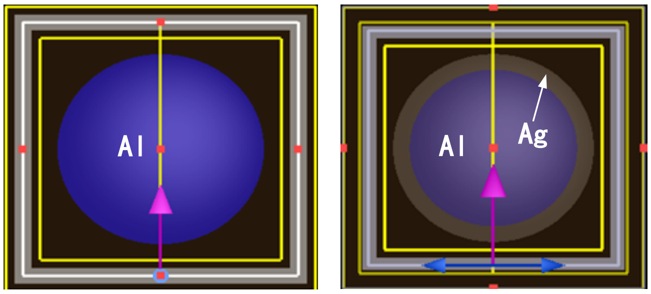
In the calculations, two physical structure models of Al nanoparticles and Al@Ag core-shell nanoparticles are established as shown in **Figure 1**. The size of the simulation region is set to 400nm*400nm*400nm, and the perfectly matched layer (PML) boundary conditions are used in x, y, and z directions. In this study, the absorption and scattering properties of nanoparticles in the UV band as well as the PV window band are mainly analyzed. Al nanoparticles do not have extinction ability for the long wavelength band, so the light source is a total-field scattered-field (TFSF) light source, with the wavelength range set as 200nm–1000nm. The polarization direction of the light source is perpendicular to the YZ cross-section, and the incident direction is perpendicular to the

XY cross-section pointing in the positive direction of the z-axis. The absorption cross-sectional area, scattering cross-sectional area, and electric field distribution of the nanoparticles were obtained by inserting a monitor.

The absorption cross-sectional area C_{abs} and scattering cross-sectional area C_{sca} of the nanoparticles are obtained by FDTD simulation, and the sum of the two is defined as the extinction cross-sectional area C_{np} of the nanoparticles.

$$C_{np} = C_{abs} + C_{sca} \qquad (1)$$

In order to characterize the extinction capacity per unit area of metal nanoparticles, the parameter of extinction cross-sectional area of nanoparticles needs to be dimensionless, and here the ratio of extinction cross-sectional area C_{np} to the cross-sectional area of the particle perpendicular to the direction of incidence of the light S_{np} (nm^2) is defined as the extinction efficiency Q_{np}, which is expressed by equation (2):



(a)A1 **(b) Al@Ag**

Figure 1. Physical models for Al and Al@Ag core-shell nanoparticles in the simulations

$$Q_{np} = \frac{C_{np}(\lambda)}{S_{np}} \qquad (2)$$

In order to ensure that enough solar radiation can reach the surface of the PV cell through the beam splitter, the volume fraction of nanoparticles in the nanofluid is generally less than 0.6%, and the scattering between particles is negligible at such a low volume fraction [20], and the extinction coefficients of the nanoparticle population are as follows:

$$\sigma_{np} = \frac{3 f_v \cdot Q_{np}}{2D} \qquad (3)$$

where, f_v is the volume fraction of nanoparticles, Q_{np} is the extinction efficiency of nanoparticles, D is the total particle size of nanoparticles (nm).

When calculating the extinction coefficient of the base solution, the scattering effect is very weak, and only the absorption of light needs to be considered, so the extinction coefficient of the base solution can be expressed as:

$$\sigma_{bf} = \frac{4\pi\kappa}{\lambda} \qquad (4)$$

where, κ represents the absorption index of the base fluid, and λ represents the wavelength of the light, where the absorption index of water in the 200nm–2500nm band is available in the optics handbook [21].

The optical properties of the nanofluid are jointly determined by the optical properties of the nanoparticles as well as the base fluid, therefore, the extinction coefficient of the nanofluid can be obtained by adding the extinction coefficient of the base fluid and the extinction coefficient of the nanoparticles:

$$\sigma_{total} = \sigma_{bf} + \sigma_{np} \qquad (5)$$

Lastly, the formula for the spectral transmittance of the nanofluid is derived from the Lambert-Beer law [22]:

$$\tau_{fluid} = \frac{I}{I_0} = e^{-\sigma_{total} \cdot L} \qquad (6)$$

where, I and I_0 are the solar radiation transmitted and absorbed by the nanofluid, respectively (W/m^2), L is the optical path (mm).

2.2. MODEL VALIDATION

Although FDTD Solutions has been widely used in the simulation of nanoscale optical components, the absorption and scattering characteristics of 60nm Al metal nanoparticles in the 200nm–1000nm band are further simulated and analyzed using FDTD Solutions in this study in order to ensure the accuracy and reliability of the calculation. The extinction efficiency of Al nanoparticles was obtained by monitoring the absorption cross-sectional area and scattering cross-sectional area in each band under vacuum background, and then the simulation results were processed to obtain the extinction efficiency of Al nanoparticles. The above calculations are validated using the classical Mie theory. It is worth noting that Mie theory is only capable of calculating the absorption and scattering properties of conventional spherical nanoparticles, whereas FDTD can calculate a wide range of complex shaped structures, which is a major advantage of the FDTD method. As shown in **Figure 2**, the maximum deviation of the calculation results of the two methods is about 2.8%, so it is reasonable and reliable to calculate the absorption and scattering characteristics of nanoparticles using the FDTD method.

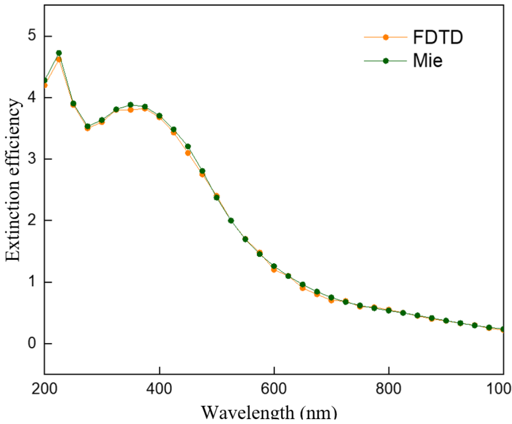


Figure 2. Comparison of the results of the FDTD method and Mie theory calculations

3. RESULTS AND DISCUSSION

3.1. EFFECT OF PARTICLE SIZE ON EXTINCTION CHARACTERISTICS OF AL NANOPARTICLES

The absorption cross-sectional area and scattering cross-sectional area of nanoparticles of six particle sizes (30nm, 40nm, 50nm, 60nm, 80nm, and 100nm) were calculated using FDTD Solutions software, and the nanoparticle extinction efficiencies were obtained using equations (1) and (2) as shown in **Figure 3**. It can be seen that the extinction efficiency curves of nanoparticles are different when the particle size of spherical Al nanoparticles is increased from 30nm to 100nm. The wavelength of the location of the resonance peak of Al nanoparticles increases with increasing particle size, indicating that the extinction properties of Al nanoparticles are affected by the nanoparticle size, which is due to the fact that the wavelength of the incident light is close to the particle size when the nanoparticles are large in size, which triggers the advanced vibrational modes of the nanoparticles. At the same time, the bandwidth of the resonance peaks increases with the particle size because different polar vibrations have different energy peaks in the nanoparticles. When a mode is excited, the bandwidth increases, which is a phenomenon known as the "hysteresis effect." In addition, it can be found that as the particle size increases to 60nm, two resonance peaks begin to appear in the figure, located at the wavelengths of 295nm and 374nm, respectively. This is because when the particle size of nanoparticles is much smaller than the wavelength of incident light, the interaction of nanoparticles with light has only dipole vibration modes, which means that there is only one dipole resonance peak on the extinction efficiency curve. However, as the particle size continues to increase, more vibrational modes at different levels are excited, such as quadrupole resonance, octupole resonance, etc.

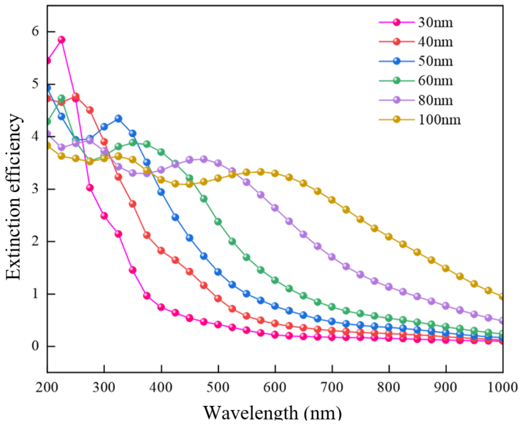


Figure 3. Extinction efficiency of Al nanoparticles at different particle sizes

Figure 4 more intuitively represents the relationship between the resonance peak position and resonance peak bandwidth of Al nanoparticles and particle size, and it can be seen that the wavelength corresponding to the resonance peak of the nanoparticles shows an approximately linear relationship with the particle size, and the wavelength of the resonance peak increases from 226nm to 576nm when the particle size is increased from 30nm to 100nm. The linear slope of the resonance peak wavelength with the increase of the particle size is about 5. The resonance peak bandwidth increases from

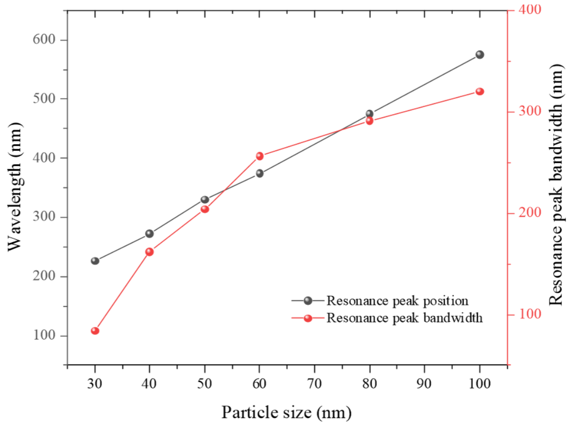
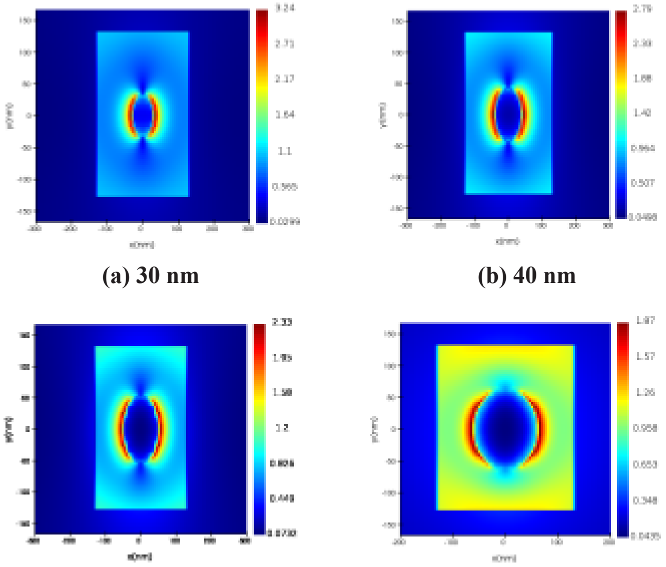


Figure 4. Resonance peak positions and resonance peak bandwidths of Al nanoparticles with different particle sizes



(a) 30 nm

(b) 40 nm

(c) 50 nm

(d) 60 nm

Figure 5. Plot of electric field distribution of Al nanoparticles with different particle sizes

84nm to 320nm, which is also nearly linear. Therefore, Al nanoparticles can produce LSPR effect in the near-ultraviolet band, and the particle size of nanoparticles affects the extinction properties of the particles. The position of the resonance peak will be red-shifted with the increase of the particle size, and the extinction intensity will be reduced. Thus, changing the particle size can play a certain role in regulating the extinction properties of nanoparticles.

Figure 5 shows the electric field distributions on the surface and in the vicinity of the spherical Al nanoparticles with different particle sizes. It can be clearly seen that a great near-field enhancement of the local equipartitioned exciton resonance effect is produced on the particle surface. This indicates that the Al nanoparticles can interact strongly with the incident light in the short wavelength band, leading to an enhancement of the local electric field, which in turn improves the absorption and scattering ability of the nanoparticles, which can also be seen from the extinction efficiency of the particles. It can be seen in **Figure 5** that the electric field strength on the particle surface decreases gradually with the increase of particle size, from 3.24 at 30nm particle size to 1.87 at 60nm particle size, which corresponds to the decrease of the maximum value of the extinction efficiency of the nanoparticles with the increase of the particle size in **Figure 3**. Therefore, when modulating the position of the resonance peaks of the nanoparticles by changing their size, it is also important to consider that the increase in particle size decreases the extinction efficiency of the particles.

3.2. EFFECT OF CORE-SHELL STRUCTURE ON EXTINCTION CHARACTERISTICS OF NANOPARTICLES

Considering that Al nanoparticles are easy to be oxidized, the dense oxide layer will affect their optical properties, and the core-shell structure nanoparticles can help to solve this problem. Meanwhile, when the core-shell of the nanoparticles are both metals, the resonance situation can lead to the electric field enhancement inside the particles, and the optical nonlinear enhancement of the composite system of bimetallic core-shell structured nanoparticles can be maximized by appropriately adjusting the core-shell ratio. For this reason, the optical properties of Al@Ag nanoparticles were investigated and the extinction efficiency of the nanoparticles was analyzed for different shell thicknesses (where the particle size of the Al core was set as 50nm and the Ag shell thicknesses were set as 2nm, 4nm, 6nm, 8nm, and 10nm, respectively). **Figure**

6 illustrates the comparisons of extinction efficiency of core-shell and single Al nanoparticles. It is shown that the extinction efficiency of nanoparticles in the 200nm–350nm band gradually decreased with the increase of the thickness of the Ag shell layer. In contrast, the extinction efficiency of core-shell nanoparticles in the 350nm–640nm band showed an opposite trend, where the extinction efficiency of the particles gradually increased with the increase in the thickness of the shell layer, and the bandwidth of the resonance peaks also gradually increased. The extinction efficiency of the resonance peak increases from 4.31 to 5.18 when the thickness of the shell layer is increased from 0nm to 10nm, but the increasing trend gradually decreases, which can be visualized in **Figure 7**.

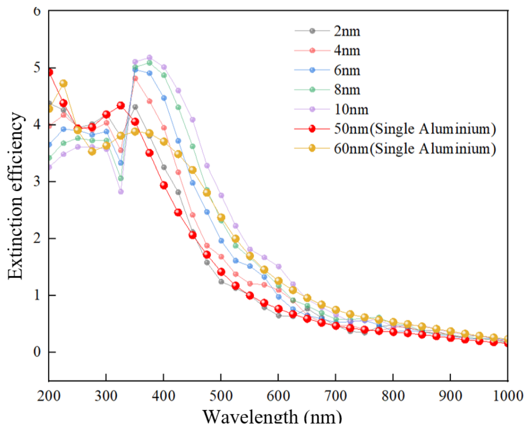


Figure 6. Extinction efficiency of core-shell and single Al nanoparticles

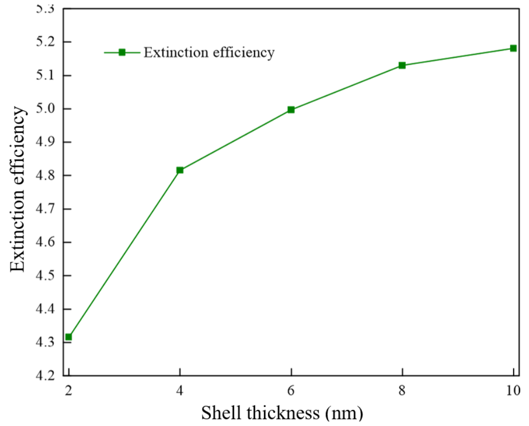
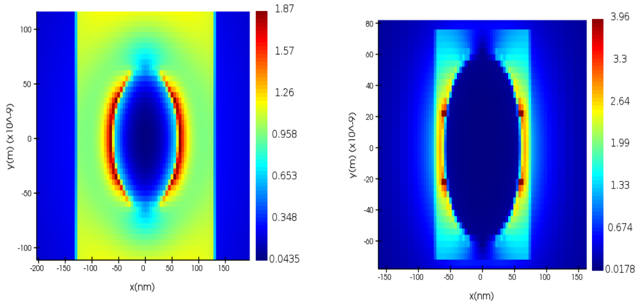


Figure 7. Resonance peak extinction efficiency of nanoparticles with different shell thicknesses

In **Figure 6**, it can be seen that the extinction efficiency of Al particles coated with Ag core-shells is significantly improved in the 350nm–640nm band compared with that of single Al nanoparticles with a particle size of 50nm. It can also be seen that the extinction efficiency of core-shell nanoparticles with a shell thickness of 10nm (total particle size of 60nm) is significantly higher than that of single Al nanoparticles with the same particle size in the 350nm–640nm wavelength band, and remains almost unchanged in the wavelength band larger than 640nm. This is the satisfactory effect, where the extinction efficiency is improved in the bands where the energy distribution is high, without affecting the high efficiency bands of photovoltaic power generation. The reason for the improved extinction efficiency of the core-shell structure can be effectively explained based on the electric field distribution in **Figure 8**. From the figure, it can be seen that the electric field strength of the core-shell nanoparticles is about twice as much as that of the single Al nanoparticles, which indicates that the nanoparticles with Ag layer achieve a near-field enhancement of the localized surface plasmon resonances, which is able to enhance interactions with the light between the nanoparticles, thus leading to the increase in the extinction efficiency of the particles.



(a) Single Al nanoparticles **(b) Core-shell nanoparticles**

Figure 8. Electric field distribution of single aluminium and core-shell nanoparticles with the same particle size of 60nm

3.3. THE SPECTRAL PROPERTIES OF NANOFLUIDS

The optical properties of nanofluids are jointly determined by the optical properties of the base fluid and the nanoparticle population. By analyzing the optical properties of nanofluids at different particle sizes and different types, it is found that the extinction properties of nanoparticles can be reflected in the optical properties of nanofluids, and the changes of particle sizes and types can cause the nanofluid transmittance to change, as shown in **Figure 9**. The variation of transmittance with wavelength of the nanofluids formed by dispersing Al@Ag with a shell thickness of 10nm, and single Al nanoparticles with particle sizes of 50nm and 60nm in water at the same optical path and volume fraction was analyzed. Upon comparison, it can be found that the spectral transmittance of the core-shell nanofluid increases near the 200nm–350nm band, and decreases near the 350nm–640nm band, with a maximum decrease of about 13% compared to the nanofluid with a 50nm particle size, and up to about 10% compared to the nanofluid with a 60nm particle size, while there is no significant change in the transmittance in the bands larger than 650nm. This indicates that wrapping Ag around the outer layer of Al enhances the extinction ability of the particles near the 350nm–650nm band, which happens to be the thermally utilized band in the ideal splitting window of the PV/T system (640–1080nm [23]), and at the same time has almost no effect on the transmittance of the photovoltaic window (640–1080nm), and thus the efficiency of the system can be effectively improved.

In addition to the effect of nanoparticles, optical path, as a factor in the propagation of light through the fluid, also affects the transmission of radiation. Generally, the greater the optical path, the more the attenuation, thus the optical path is also one of the important parameters affecting the optical properties of the nanofluid. As shown in **Figure 10**, the spectral transmittance of nanofluids at different optical paths (10mm, 30mm, and 50mm, respectively) was analyzed at a constant nanoparticle size of 60nm and a nanofluid volume fraction of 0.6%. It can be found that the spectral transmittance of the nanofluid decreases in the whole band with the increase of the optical path, which is consistent with the greater attenuation of electromagnetic wave radiation with the larger optical path. Meanwhile, it can be seen in **Figure 10** that pure water has almost no extinction ability for light in the 300–700nm band, so the decrease in the transmittance of nanofluid in this band is determined by the extinction performance of nanoparticles. The extinction efficiency of Al nanoparticles in the rest of the band is very low, and the trend of the curve coincides with the trend of the transmittance of pure water. Therefore, the addition of Al nanoparticles in water reduces the spectral transmittance of the photothermal window (200nm–640nm) in a wide range, which can effectively reduce the radiation reaching the PV panels, decrease the heat reaching the unavailable wavelengths of the PV cells, and lower the surface temperature of the PV modules.

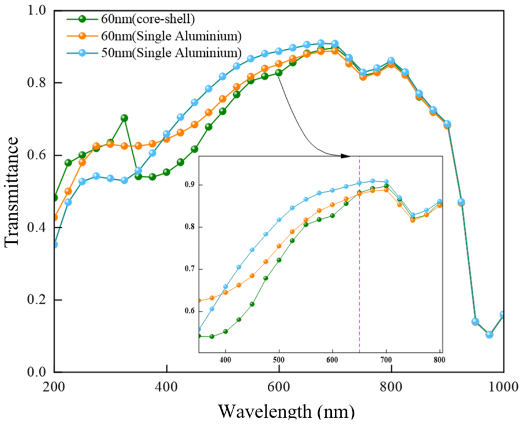


Figure 9. Spectral transmittance of nanofluids with different structures and particle sizes

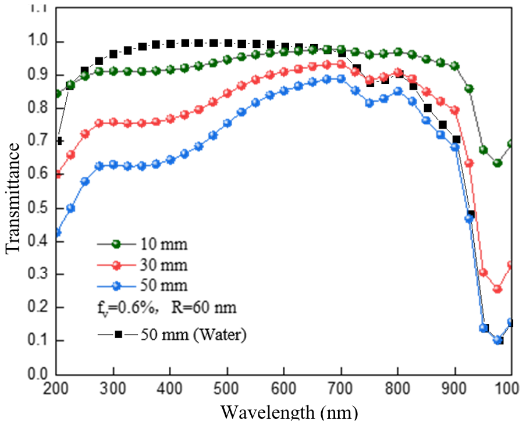


Figure 10. Spectral transmittance of nanofluids and pure water at different optical path

The volume fraction of nanoparticles also influences the optical properties of the nanofluid. **Figure 11** shows the spectral transmittance of nanofluids with different volume fractions by varying the volume fraction of nanoparticles in the nanofluid by 0.6%, 0.5%, and 0.4% while keeping the nanoparticle particle size (60nm) and optical path (30mm) constant, respectively. It is found that the spectral transmittance of the nanofluid in the 200–700nm band decreases gradually with the increase of the volume fraction of nanoparticles in the nanofluid, and the transmittance in the photovoltaic window band decreases very little. This is determined by the extinction properties of Al nanoparticles, and increasing the volume fraction of the particles increases the concentration of the nanofluid and enhances the extinction properties of the particles. On the other hand, the spectral transmittance in the long wavelength band (700–1000nm) hardly changes, which is due to the weak extinction ability of Al nanoparticles in this band, coupled with the constant optical path, and therefore reflects the optical properties of the base liquid (water). Overall, increasing the volume fraction of nanoparticles decreases the spectral transmittance of the nanofluid at short wavelengths, while it ensures higher transmittance in the photovoltaic window band. Therefore, a higher volume fraction should be ensured as much as possible when using Al nanofluids as a beam splitter.

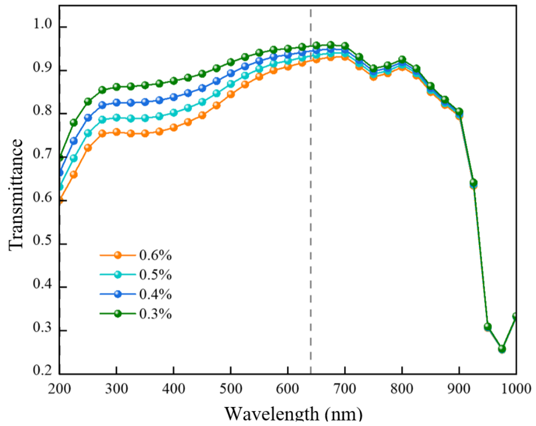


Figure 11. Spectral transmittance of Al nanofluids with different volume fractions

4. CONCLUSION

In this paper, the extinction properties of Al nanoparticles with different sizes and structures were analyzed using the FDTD method, and it was found that the resonance wavelength of Al nanoparticles would be red-shifted with the increase of the particle size and the resonance peaks would be broadened. The change of the particle size could regulate the extinction properties of Al nanoparticles. In order to optimize the optical properties of Al nanoparticles and to solve the problem of their susceptibility to oxidation, the extinction properties of Al@Ag nanoparticles with core-shell structure were designed and analyzed. It is found that the interaction between the particles and light is improved in the core-shell structure, which enhances the extinction ability of the nanoparticles, but the increase in the extinction efficiency of the particles slows down with the increase in the thickness of the shell layer. By dispersing Al and Al@Ag nanoparticles into water to form nanofluids, it is found that the spectral transmittance of both Al and Al@Ag nanoparticles is effectively reduced in the short wavelength band compared to that of pure water. Moreover, the core-shell structure reduces the transmittance in the 350–650nm band by up to 13% and 10% compared to single Al particles with particle sizes of 50nm and 60nm, while it has almost no effect on the transmittance in the photovoltaic window (640–1080nm). Therefore, the efficiency of the PV/T system can be effectively improved by effective modulation of Al nanoparticles.

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DISCLOSURE STATEMENT

The authors declare no conflict of interest.

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