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Experimental Research on the Selective Absorption of Solar Energy by Hybrid Nanofluids

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Abstract: As low-cost, widely distributed and easily accessible renewable clean energy, solar energy has attracted more and more attention. Direct absorption solar collectors can convert solar energy into heat, but their efficiency is closely related to the absorption performance of the working fluid. In order to improve the absorption efficiency of direct absorption solar collectors, an experimental study on the selective absorption of solar energy by hybrid nanofluids was carried out. Five hybrid nanofluids were prepared and characterized, and the energy transfer advantages of hybrid nanofluid over single nanofluid were carefully studied. Experiments have found that the light-to-heat conversion properties of hybrid nanofluids show no obvious advantages or disadvantages compared with single nanofluid, and their performance is closely related to the types of nanoparticles. In addition, the hybrid nanofluid generally has two peaks, exactly the same as the single nanofluid in the mixed component, but the absorption curve is flatter than that of the single nanofluid. Further research of more types of hybrid nanofluids can provide new insights into the use of solar energy.

Keywords: nanofluids; solar energy; photothermal conversion efficiency

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1. Introduction

With the increase of energy demand, the dominant energy composition will be transformed from traditional fossil energy to non-fossil new energy. As a kind of renewable clean energy with wide distribution, simple acquisition and low cost, solar energy has attracted more and more attention in industrial application and scientific research. Solar energy can be converted into heat energy by direct absorption in a solar collector, whose efficiency is closely related to the absorptivity of the working fluid. Today, it is still a huge challenge how to improve the efficient and extensive use of solar energy.

In 1995, Choi et al. [1] of Argonne National Laboratory in the U.S. put forward the concept of nanofluid for the first time in the world. The so-called nanofluid refers to the dispersion of metal or non–metal nanoparticles or nanotubes into traditional heat transfer media, e.g., water, oil and alcohol to prepare a new uniform and stable medium with high thermal conductivity, which is an innovative application of nanotechnology in the traditional thermal engineering field. This concept brings new hope to the research of enhanced heat transfer technology. It is found that due to the small size effect and Brownian motion, the nanofluids prepared with nanomaterials have stronger suspension stability, excellent heat transport performance and spectral absorption performance than the traditional fluids with micron or millimeter solid particles. Based on that, a large number of researchers have proposed to use nanofluids as the circulating working medium to enhance the photothermal conversion efficiency of solar energy in direct absorption solar collectors. For traditional solar thermal collectors (STC), the solar energy is absorbed firstly by the engineered solid surface, which is normally coated by high absorption materials. Then, the absorbed solar energy will be transferred through thermal conduction from the working fluid. Conversely, the direct absorption solar collector (DASC) does not absorb solar energy through the surface, the properly selected nanoparticles will absorb the solar energy volumetrically, which means the solar energy will be trapped inside the working fluid. This volumetric absorption process addresses the limitation of the surface heat transfer process, which is normally associated with conventional STCs, considerably increasing the photothermal conversion efficiency by selecting the absorption spectrum [2–5]. Metal nanoparticles (e.g., Ag and Au) have been extensively investigated owing to their surface plasmon resonance effect [6–9]. In addition, the photothermal conversion efficiency of nanoparticle–based work fluid has been investigated by many researchers. Otanicar et al. [10] compared different nanofluids, including carbon–based and metal– based nanoparticles. The conclusion was that many characters can affect the solar harvesting efficiency, especially the nanoparticle size, material and the volume concentration. Moreover, the photothermal conversion efficiency was increased by 5% when compared with the standard working fluid (i.e., water).

In the recent years, the related research mainly focused on experimental studies on the photothermal conversion characteristics of single nanofluids, such as carbon nanotubes, graphite, Au, Ag, Cu and other nanofluids [11–15]. It is found that the absorptivity of the direct heat absorption solar collector with nanofluid is higher than that of the traditional working medium, which is mainly affected by the photothermal conversion characteristics of the nanofluid. Due to the polariton effect of plasma, the absorptivity of noble metal nanomaterials, such Au, Ag and Cu, in the visible light range and even in the infrared region is higher than that of non–metallic nanomaterials. For instance, gold nanofluids have excellent solar energy absorptivity because of its plasmon resonance characteristics on the local surface. The absorption peak of gold nanofluids for solar energy is concentrated at 520 nm, and the absorption efficiency of gold nanofluids for solar energy will decrease significantly when the wavelength is greater than 600 nm. The absorption peak of silver nanofluids is concentrated at 410 nm, and when the wavelength is greater than 650 nm, the absorption efficiency of silver nanofluid for solar energy will also decrease significantly. The solar radiation energy is mainly concentrated in the wavelength range of visible light and infrared light, which is between 200 nm and 3000 nm. Therefore, in order to achieve the efficient absorption of solar radiation energy by nanofluids in the full wavelength range, it is considered to mix gold and silver nanofluids to construct gold–silver hybrid nanofluids, and to examine whether they could achieve the absorption characteristics of gold and silver single nanofluids at the same time.

Karami et al. [16] prepared an alkaline carbon nanotube (f–CNT) aqueous solution to study the thermal conductivity, optical properties and dispersion stability of f–CNT. The results show that even at low concentration, the extinction coefficient of alkaline carbon nanotube solution is significantly improved compared with the base solution. When only 150 ppm nanoparticles are added, the thermal conductivity of the fluid is enhanced by 32%. The results also show that the f–CNT aqueous solution can effectively enhance the overall efficiency of DASC. Chen et al. [17–19] proposed and verified the creative idea of enhancing the photothermal conversion efficiency of the solution with plasma nanoparticles (PNP). They used an improved citric acid reduction method to prepare gold nanofluid (GNP) as a sample to illustrate the photothermal conversion performance of plasma nanoparticles in a sunlight simulator. The results show that gold nanofluids have the strongest photothermal conversion efficiency compared with other nanofluids. When the solution concentration is as low as 0.15 ppm, the photothermal conversion efficiency of gold nanofluids relative to the base solution is increased by 20%, and the specific absorption efficiency reaches 10 kW/g. In addition, even if GNPs are still in an independent scattering mechanism, the concentration of nanofluids will be enhanced, and the photothermal conversion efficiency will increase, but the specific absorption (SAR) shows a reverse trend. Filho et al. [20] studied the photothermal conversion characteristics of silver nanofluids in a real environment. A stable silver nanofluid was generated by a high–pressure homogenizer and then placed on the roof under sunshine for 10 h. The results show that the silver nanofluid with low concentration also has high photothermal conversion ability. The solar energy absorbed by the silver nanofluid with concentration of 6.5 ppm is increased to 144% relative to the base solution at the peak temperature, which is due to the low heat loss generated by the silver nanofluid during the initial radiation and the strong plasma resonance effect on the surface. In addition, the photothermal conversion characteristics of silver nanofluids show transient behavior. In the range of nanofluid concentration of 6.5 ppm, the SAR of the fluid remains almost unchanged at 0.6 kW/g, but it decreases significantly at higher concentration, which could be owing to the increase of the interaction force between nanoparticles. He et al. [17–19,21] prepared Cu nanofluids by the two–step method. Based on the integrating sphere principle, the absorption spectra of nanofluids in the wavelength range from 250 nm to 2500 nm were measured with an ultraviolet–visible–near–infrared (UV–Vis–NIR) spectrophotometer. They investigated the effects of particle size, mass fraction and optical path on the transmittance of nanofluids. The extinction coefficient and photothermal conversion characteristics of nanofluids were investigated theoretically and experimentally. The results show that with the increase of particle size, mass fraction and optical path, the transmittance of Cu nanofluids reduces. The maximum temperature of 0.1 wt% Cu nanofluids absorbing solar energy is 25.3% higher than that of deionized water. Khullar et al. [5,22] compared the efficiency differences of solar energy absorption between nanofluids and traditional materials through quantitative experiments, including amorphous carbon nanoparticles distributed in ethylene glycol solution, carbon nanotube particles distributed in deionized water and traditional commercial materials (coated copper substrate). The results show that the absorption performance based on nanofluid is more efficient, and the volume fraction which produces the highest efficiency was found. Under similar operating conditions, if electromagnetic radiation is allowed to directly contact a large area of fluid, a higher average stagnation temperature can be achieved, which can be attributed to the high light energy efficiency and radiation energy conversion efficiency of nanofluids. In addition, the performance of the system is affected by the volume fraction of the nanofluid. The limit state is close to surface absorption at high volume fraction. In addition, they also found that, consistent with the basic theory of volume absorption, the temperature distribution in space is nearly consistent. In order to evaluate the efficiency of direct absorption solar collectors based on different kinds of nanofluids, Zhang et al. [23] experimentally studied the photothermal conversion characteristics of Au, Si, Fe_3O_4, Al_2O_3 and diamond nanofluids under the same experimental setting. The results show that the photothermal conversion efficiency of the fluid is greatly affected by the addition of nanoparticles, and the enhancement degree of the nanofluid is as follows: Al_2O_3, diamond, Si, Fe_3O_4 and Au. For a certain total mass concentration, it is found that the efficiency of Fe_3O_4–Au nanofluid is greater than that of pure single Au nanofluid.

In addition, the photothermal conversion characteristics of nanofluids are closely related to the concentration of nanofluids. In a certain concentration range, the higher the concentration is, the higher the absorption efficiency could be reached. It is also found that different kinds of nanofluids have different absorption peaks and different wavelength ranges. To sum up, most studies mainly focus on the heat absorption efficiency of DASC using single nanofluids, and there is insufficient research on the solar absorption performance of hybrid nanofluids. In addition, there is an absorption peak in the absorption of solar energy by a single type of nanofluid, and the absorption effect is significant only in a narrow specific spectral range; so, it is difficult to achieve efficient absorption in the full wavelength range of solar radiation. Therefore, the idea of using hybrid nanofluids in DASC is proposed to further enhance the photothermal conversion efficiency of direct absorption of solar energy, especially to improve the solar energy absorption efficiency of nanofluids in the full wavelength range. By preparing and characterizing different hybrid nanofluids, the radiation characteristics and photothermal conversion efficiency of mixed nanofluids are experimentally studied, which provides a new direction for the design of nanofluids to efficiently absorb and convert solar energy.

2. Preparation and Characterization of Nanofluids

2.1. One–Step Method to Prepare Gold Nanofluids

The one–step method of nanofluid preparation refers to the simultaneous completion of the preparation process of nanoparticles and the dispersion process of nanoparticles in the base solution. The preparation of gold nanofluid requires magnetic stirring and reduction reaction through citrate. The detailed information can be seen in our previous research [2,3,12,13]. The specific process is as follows:

(1) Take 100 mL of aqueous $HAuCl_4$ (tetrachloro auric acid) solution with a concentration of 5 mM, turn on the electromagnetic heating agitator and stir the solution evenly and heat it until the solution boils;
(2) Keep the $HAuCl_4$ solution in the state of vigorous boiling and uniform stirring, quickly add 100 mL of 10 mM trisodium citrate aqueous solution, observe and record the change of solution color and time in the bottle;
(3) Continue stirring and heating until the solution boils. After 10 min, turn off the heating power and stop heating. Add and continue stirring and cooling for 15 more minutes, and observe and record the color change of the solution.

After completing the above steps, the sample solution was transferred to a clean 100 mL bottle for storage, that is, the original gold nanofluid is prepared.

The colloidal solution of metal nanoparticles prepared according to the above method was photographed at 200 kV by TECNAI G2 F20 S–twin field emission transmission electron microscope (TEM), and at 120 kV by JEM–1200EX field emission scanning electron microscope (SEM). The results are shown in Figures 1 and 2. It can be seen that most of the small–size gold nanoparticles are spherical, while the larger size particles are oval, with an average size of about 12–15 nm.

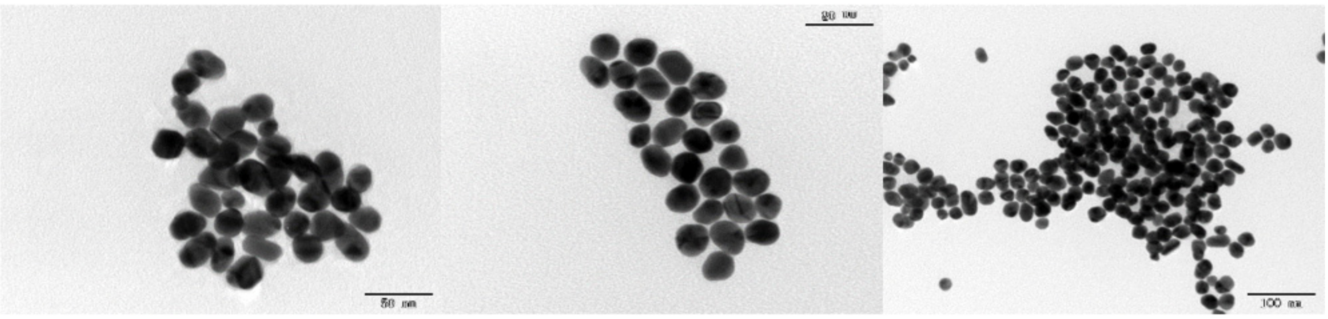

Figure 1. TEM images of Au nanofluids.

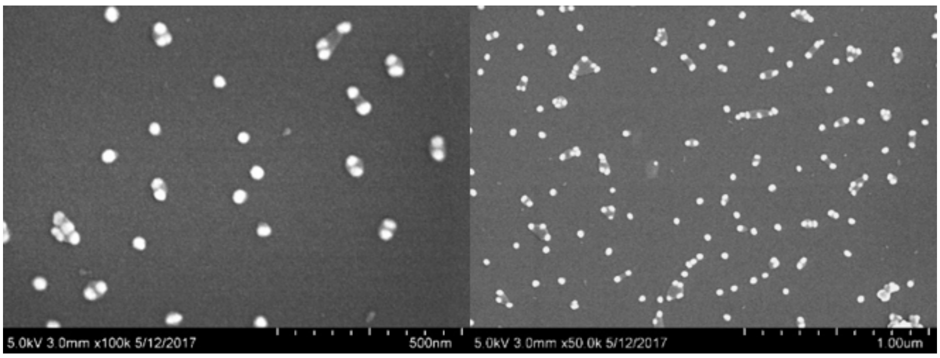

Figure 2. SEM images of Au nanofluids.

2.2. Two–Step Method to Prepare Other Nanofluids

The Two–step method of nanofluid preparation refers to dispersing the prepared nanoparticles into the base fluid, and the preparation and dispersion process is carried out in two steps. The specific operation of preparing Ag, Cu, TiO_2, Al_2O_3, SiO_2, multi–walled carbon nanotubes (MWCNT) and other nanofluids is as follows.

Add an appropriate amount of dispersant and a certain amount of deionized water in a beaker, put a certain amount of nano–powder particles weighed with use HK14F8033762 electronic balance into deionized water, stir the solution and put it in a FB11207 ultrasonic water bath with an ultrasonic frequency of 40 KHz for ultrasonic vibration. Then, use an ultrasonic breaker for stirring. After a period of time, the product can be prepared. The electron micrograph of the required nanofluid is shown in Figure 3.

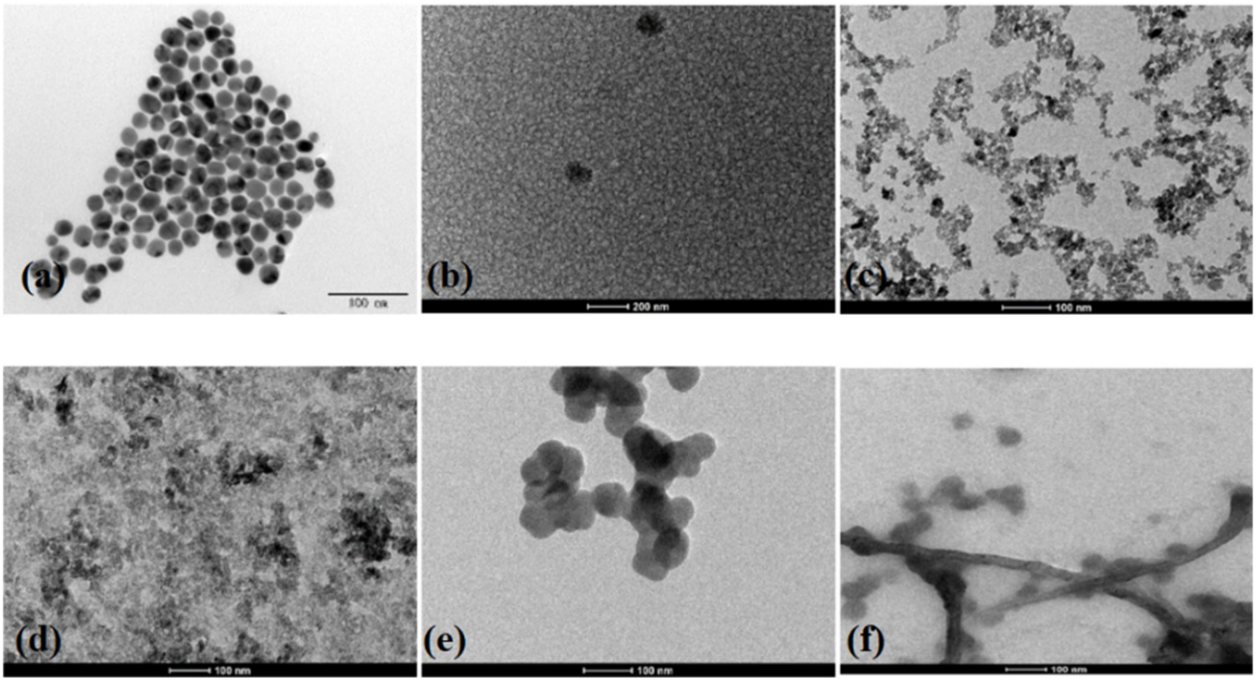

Figure 3. TEM images of six nanofluids (**a**) Ag (**b**) Au (**c**) TiO_2 (**d**) Al_2O_3 (**e**) CuO (**f**) MWCNT.

2.3. Preparation and Characterization of Hybrid Nanofluids

By mixing the above seven prepared nanofluids, five mixed nanofluids are finally obtained, including Au–Ag, Au–Cu, Au–MWCNT, Au–Al_2O_3, CuO–TiO_2, etc., as used in the experiments. The TEM image is shown in Figures 4–8.

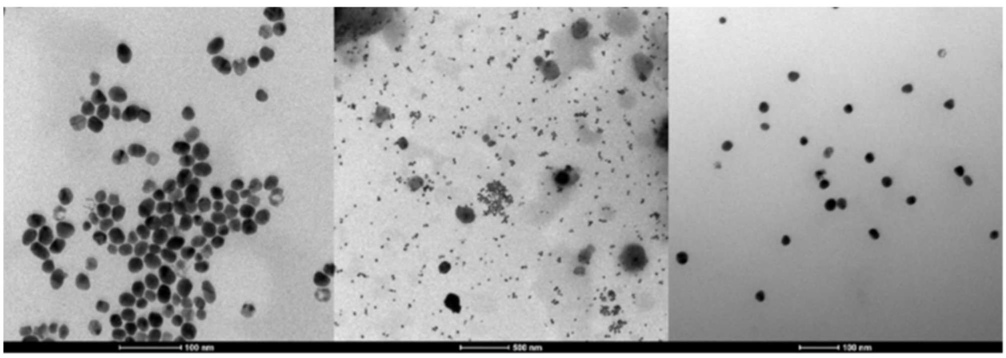

Figure 4. TEM image of Au–Ag hybrid nanofluid.

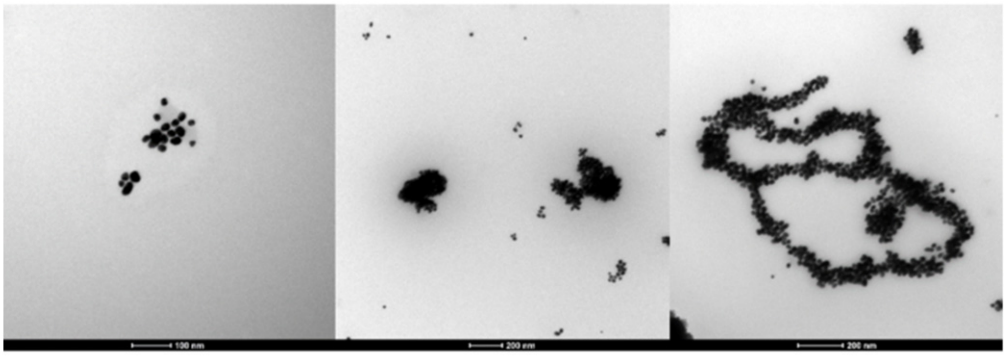

Figure 5. TEM image of Au–CuO hybrid nanofluid.

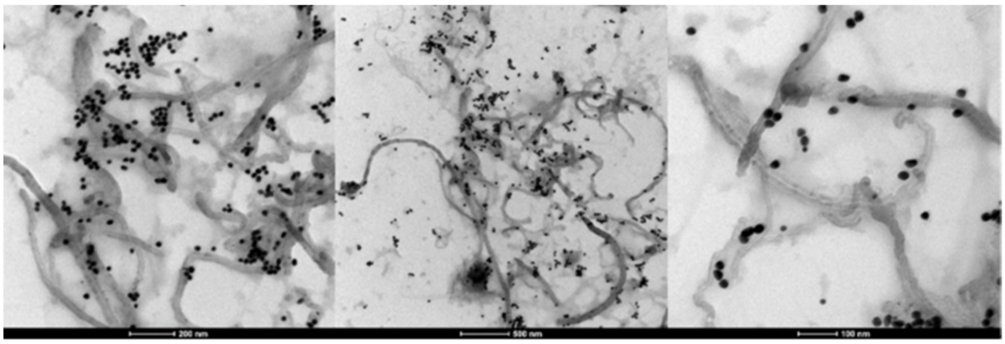

Figure 6. TEM image of Au–MWCNT hybrid nanofluid.

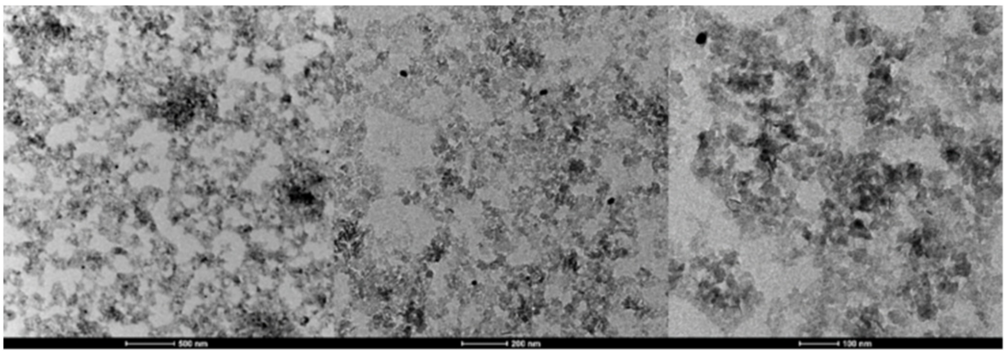

Figure 7. TEM image of Au–Al_2O_3 hybrid nanofluid.

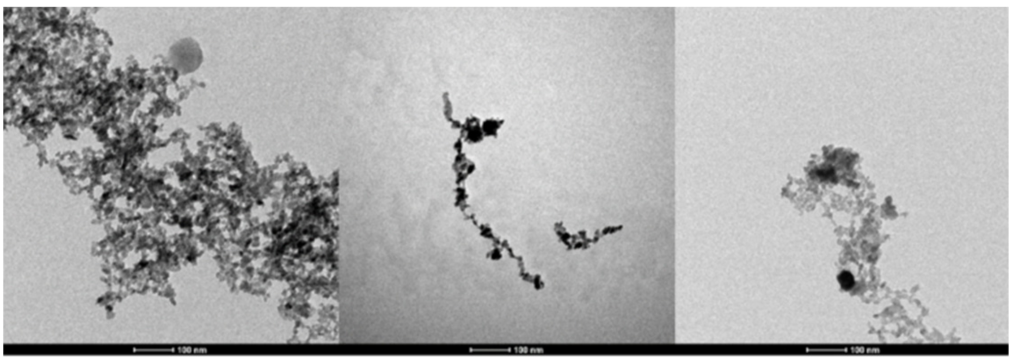

Figure 8. TEM image of CuO–TiO_2 hybrid nanofluid.

The hybrid nanofluids can be seen in Table 1, where Au nanofluid can also be called GNPs nanofluid.

Table 1. The list of hybrid nanofluid.

	Au	**Ag**	**TiO_2**	**Al_2O_3**	**CuO**	**MWCNT**
Au (i.e., GNPs)	✓	✓		✓	✓	✓
Ag	✓	✓				
TiO_2			✓		✓	
Al_2O_3	✓			✓		
CuO	✓		✓		✓	
MWCNT	✓					✓

At first, the solutions were processed at 50% power for 2 h with an Ultrasonic Cell Disruption (UCD) System (ThermoFisher Scientific, FB705). In the next step, the nanofluids were standing for 2 months. Finally, the absorbance of nanofluids were measured to compare the changes by a UV–spectrophotometer (Shimadzu UV–1800). The results showed that the difference of absorbance before and after standing for 2 months was less than 1%, i.e., the nanofluids maintained good stability.

Many researchers reported that the thermal conductivity could be enhanced when nanoparticles were seeded into the fluid. It was worth noticing that the volume concentration of nanoparticles was higher than 100 ppm, normally 1000 ppm. The high concentration resulted in the thermal conductivity change, when nanoparticles participated in the heat transfer process. However, the thermal conductivity of the nanofluids (and hybrid nanofluids) was almost the same with the base–fluid (i.e., water). No enhancement was reported for the current experimental test. The thermal conductivity was tested by KD–2 Pro (Decagon Instrument, Inc., Pullman, WA, USA). The reason for this was that the volume concentration in this research was less than 50 ppm. The diluted concentration of the nanofluid limited the enhancement of thermal conductivity caused by nanoparticles.

3. Experimental Setup

As shown in Figure 9, six groups of sample solution were injected into the glass tube at a time, 5 mL different kinds of nanofluid were injected into each group sample in the experiment. Temperature values of the nanofluid in the glass tube were measured when the temperature rose after absorbing solar energy and reached a steady state. Therefore, a type T thermocouple and a temperature data collector were used to measure it. A total of seven temperature collection points was set, and the top of six thermocouples were fixed at the 2.0-mL position on the scale of the glass tube. One thermocouple was exposed in the environment to measure the ambient temperature. The uncertainty of these thermocouples is ±0.5 °C. The data were recorded in the connected computer LabVIEW through the data collector to realize the real–time display and storage of the data. In the experiment, the regional temperature at the same time was measured and visually shown with the Tix640 infrared thermal imaging camera of the Fluke Company of the United States.

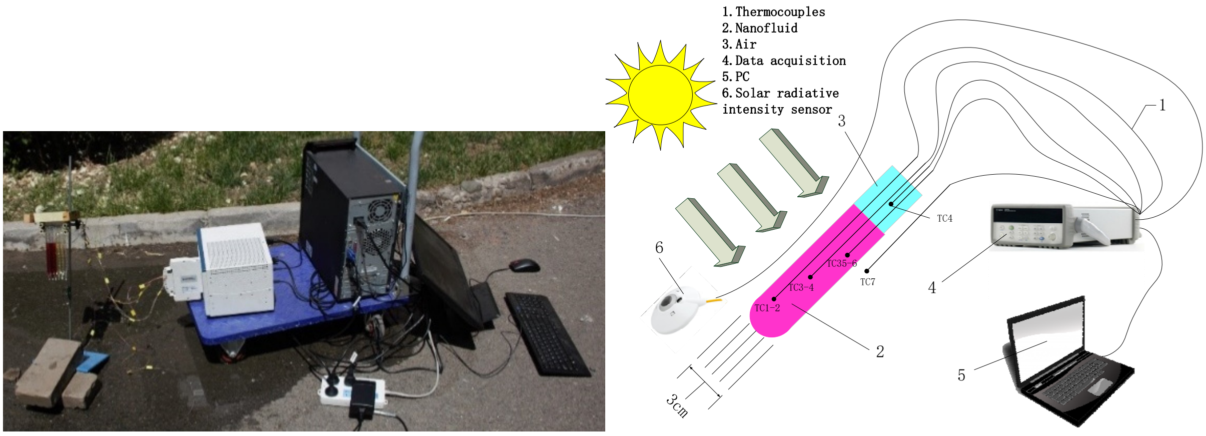

Figure 9. Experimental Setup and diagram of the experimental setup.

4. Theoretical Calculation of Nanofluid Absorbing Solar Energy and Heat Conversion Efficiency

For the nanoparticles studied in the experiment, according to the Mie scattering theory, the radiation transmission process of sunlight to the nanofluid can be approximated as a one–dimensional heat conduction problem. An analytical solution to the radiation equation can be obtained as:

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

where E represents the spectral emission power. Since the upper limit of the ultraviolet–visible–near–infrared spectrophotometer is less than 1 µm, the formula can be simplified to:

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

This simplification has been explained in our previous work [2–4,12,13,24]. From this equation, the abruption coefficient can be calculated through the absorbance (i.e., A_λ) from the UV spectrophotometer.

This is the derivation process of the Beer–Lambert law. Based on that, a new calculation method is proposed to calculate the theoretical maximum light–to–heat conversion efficiency, which is the total absorption efficiency of a nanofluid at a given optical thickness and nanoparticle concentration.

$$\eta(\mathrm{L}, f_v) = \frac{\int_0^R \int_{0.2\mu m}^{3\mu m} \mathrm{E}_0(\lambda)(1 - 10^{-A(\lambda)\frac{L}{L_0}}) d\lambda dr}{R \int_{0.2\mu m}^{3\mu m} \mathrm{E}_0(\lambda) d\lambda} \tag{3}$$

where R is the radius of the glass tube. The calculated wavelength is between 200 nm and 3000 nm, and there is 95% of the solar radiant energy in this wavelength range.

5. Results and Discussion

5.1. Absorption of Solar Energy by a Single Nanofluid

According to the above theoretical formula, the absorption efficiency of different types of nanofluids can be calculated and the results are shown in Figure 10. The input data are the absorbance (i.e., A_λ) from the UV spectrophotometer and the radius (i.e., R) of the testing tube. According to Equation (3), the absorption efficiency can be determined. It can be seen from the figure that the absorption efficiency of the Au, Ag, Cu, Al_2O_3, CuO, TiO_2, TiO_2, MWCNT single nanofluid is 48.67%, 29.11%, 29.39%, 67.69%, 48.19%, 38.62%, and 67.16%, respectively.

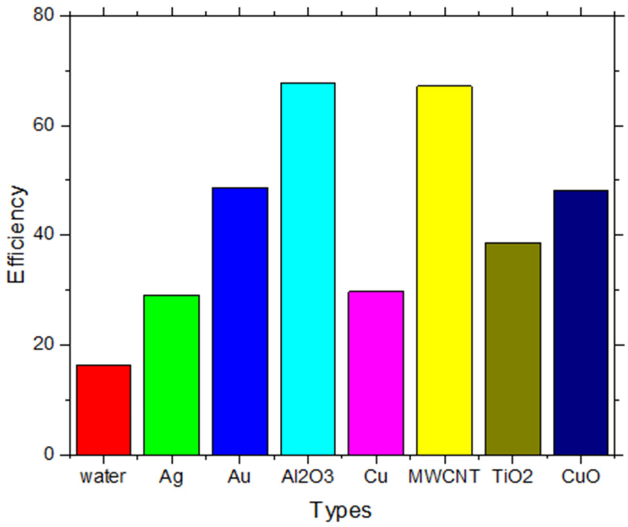

Figure 10. Absorption efficiency of a single nanofluid.

The experiment measured the absorption spectra of five silver nanofluids with different concentrations to study the absorption characteristics of one single nanofluid with different concentrations. The 30% silver nanofluid was diluted 5 times, 10 times, 30 times, 90 times and 180 times, respectively, and the absorption spectra were measured with the UV–Vis–NIR spectrophotometer. Equation (3) was used to process UV to get the predicted solar energy absorption efficiency. The results are shown in Figure 11.

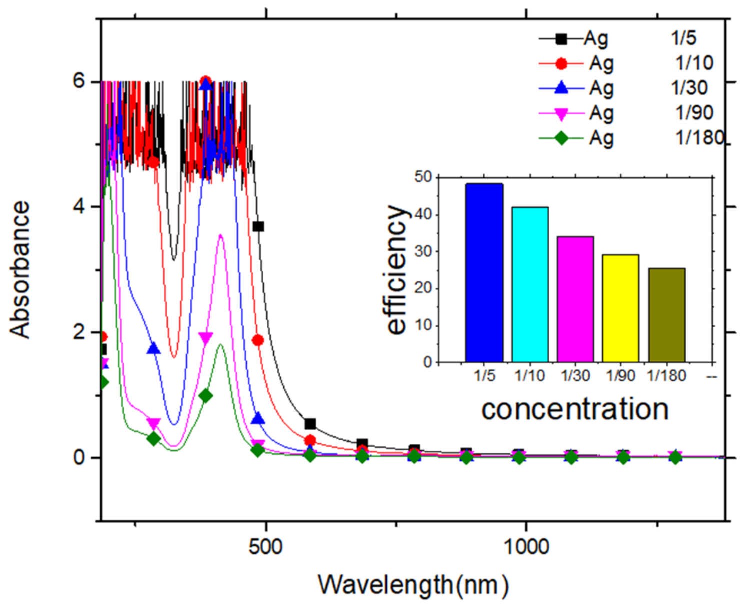

Figure 11. Absorption spectra of silver nano–solutions with different concentrations and prediction of solar energy absorption efficiency.

As shown in Figure 11, the absorption efficiency decreases with the decrease of concentration, and the calculated predicted absorption efficiencies are, respectively, 48.29%, 42.04%, 33.95%, 29.11% and 25.62%. However, it can be seen from the absorption spectrum between from 200 nm to 3000 nm, the absorption troughs of silver nano–solutions with different concentrations are all around 325 nm. In addition, the peaks are at 458 nm, 402 nm, 416 nm, 414 nm and 413 nm, respectively. Clearly, the shifts are related to the size change of the nanoparticles, which is acceptable when all are distributed near the theoretical value of 420 nm. The results show that the concentration has no effect on the wavelength range of the absorption peak. At the same time, the silver nanofluid has a significant absorption effect only in a specific narrow spectral range, and the absorption efficiency of the silver nanofluid beyond 700 nm is very weak, regardless of the concentration. These results are consistent with the results described in the literature.

In general, the solar spectral absorption property of nanofluids, which is influenced by the shape of the particle materials and the concentration of suspended particles, determines its solar photothermal conversion performance. In addition, the solar thermal conversion performance of nanofluids is more or less higher than that of basic fluids, i.e., deionized water. This is because the nanoparticles dispersed in water have a strong absorption of sunlight, and the optical path of photons entering nanofluids can be enhanced by the scattering effect between nanoparticles, which is conducive to the absorption of sunlight.

5.2. Absorption of Solar Energy by Hybrid Nanofluids

The absorption spectrum of the hybrid nanofluid was measured with the UV–Vis–NIR spectrophotometer, and then, the data were calculated using a simplified model that predicts the solar thermal conversion characteristics of the nanofluid. The results are shown in Figure 12.

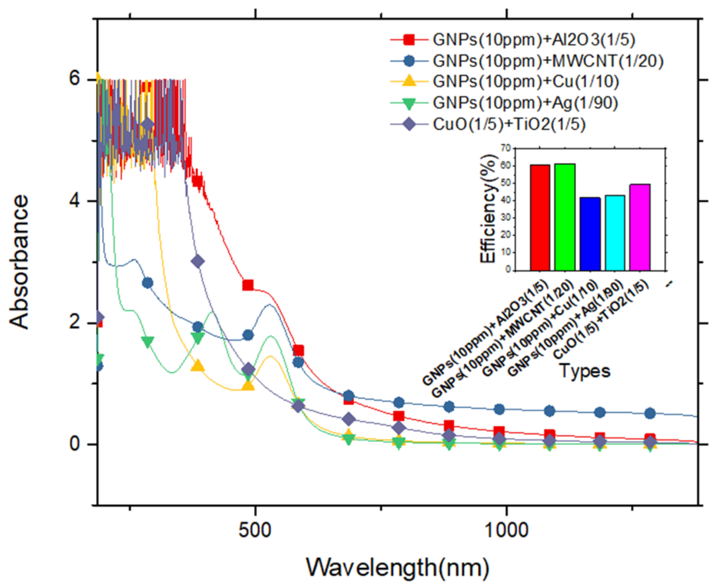

Figure 12. The absorption spectrum and light–to–heat conversion efficiency of the hybrid nanofluid.

The absorption efficiency of all nanofluids within the wavelength between 200 and 3000 nm is calculated by the Equation (3). The calculation results of the light–to–heat conversion efficiency of GNPs (10 ppm) +MWCNT (1/20), GNPs (10 ppm) +Al_2O_3 (1/5), GNPs (10 ppm) +Ag (1/90), GNPs (10 ppm) +CuO (1/10), CuO (1/5) +TiO_2 (1/5) are 61.34%, 60.75%, 42.84%, 41.67%, 49.36%, respectively. Combining the calculation results from Figure 12, the following conclusions can be obtained:

(1) Most of the hybrid nanofluids have an infrared absorption curve close to zero, but the Au–MWCNT hybrid nanofluids still have a certain absorption capacity for sunlight beyond 760 nm.

(2) The hybrid nanofluids containing gold have absorption peaks around 520 nm. The order of the solar absorption peaks of the hybrid nanofluids between 400 nm and 700 nm is: Au–Al_2O_3, Au–MWCNT, Au–Ag, Au–Cu. Among them, the Au–MWCNT and Au–Ag hybrid nanofluids even show two fluctuations with two absorption peaks.

(3) The absorption curve of the hybrid solution of CuO and TiO_2 is more uniform, with a high absorption efficiency in the full spectral range with no absorption peak, and

gradually decreases with the increase of wavelength, but the absorption efficiency of the hybrid nanofluid is still higher than that of the Au–Ag and the Au–Cu nanofluids.

In the previous theoretical research, it was found that the gold nanofluid has a high light–to–heat conversion efficiency, so a large number of gold nanofluids were used in the experiment. The absorption spectra and absorption efficiencies of the 10 ppm and 5 ppm gold nanofluids used are shown in Figure 13.

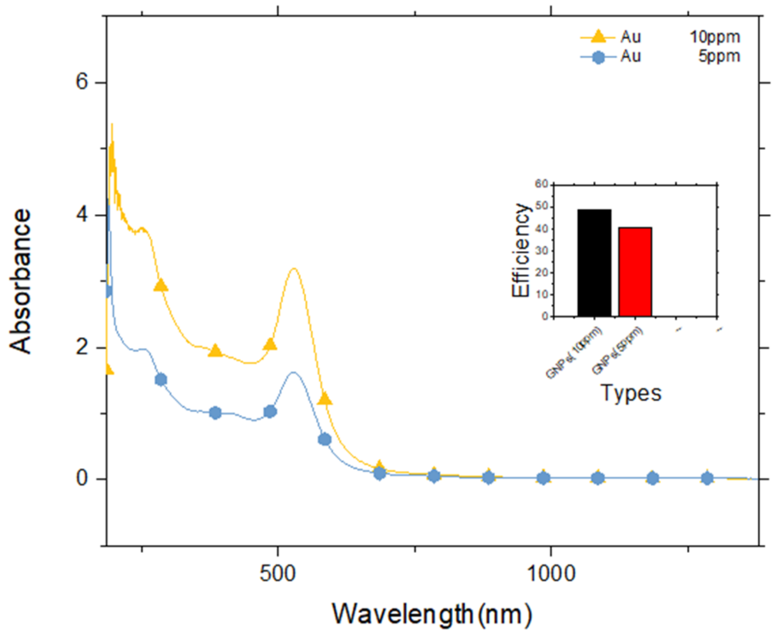

Figure 13. Absorption spectrum and absorptivity of gold nanofluid used in the experiment.

From Figure 13, the absorption peak of the gold nanofluid is 520 nm, and the absorption efficiency significantly decreases after 760 nm. Increasing the concentration of the gold nanofluid can enhance the absorption efficiency. The calculated absorption efficiency of the 10 ppm gold nanofluid is 48.67%, and the absorption efficiency of the 5 ppm gold nanofluid is 40.57%. Doubling the concentration, the absorption efficiency of the gold nanofluid only increased by 8.1%, so it is not practical for engineering applications from the economic point of view. However, when mixing gold with different nanoparticles, the enhancement of absorption efficiency is different. The absorption efficiency is increased by 12.67% for the Au–Al_2O_3 hybrid nanofluid, 12.08% for the Au–MWCNT hybrid nanofluid, 5.83% for the Au–Ag hybrid nanofluid, and 7% for the Au–Cu hybrid nanofluid. In addition, according to Figure 12, it is found that the absorption efficiency of a single Al_2O_3–MWCNT in the full spectrum is higher. Therefore, it is still necessary to be cautious when selecting mixed materials, and it is necessary to consider the absorptivity of a single mixed component in the full spectrum.

After comparing the absorption properties of different single nanofluids, it is still necessary to compare the absorption capacity changes of the hybrid nanofluids with respect to the single nanofluid before mixing. Figure 14 is obtained by calculating the absorptivity of all experimental samples mixed with gold. Results show that if two single nanofluids both have a higher absorption efficiency in the full spectrum range, when they are mixed with the same volume, the resulting mixed fluid may have a higher absorption efficiency. For instance, the wavelengths of the absorption peaks of TiO_2 and CuO are 531 nm and 750 nm, respectively, and the absorption efficiency of them is 38.62% and 48.19%, respectively, and the absorption efficiency of the mixed solution is as high as 49.36%. However, if two nanofluids have similar absorption spectra, the efficiency of the resulting hybrid nanofluid may be relatively low. Taking the Au and TiO_2 mixtures as an example, they have similar absorption spectral characteristics between 300 nm and 100 nm.

The absorption efficiency of Au nanofluid is 48.67% and is 67.69% for TiO_2, however, the absorption efficiency after mixing is 60.75%, which is close to the absorption efficiency of the Al_2O_3 solution after double dilution.

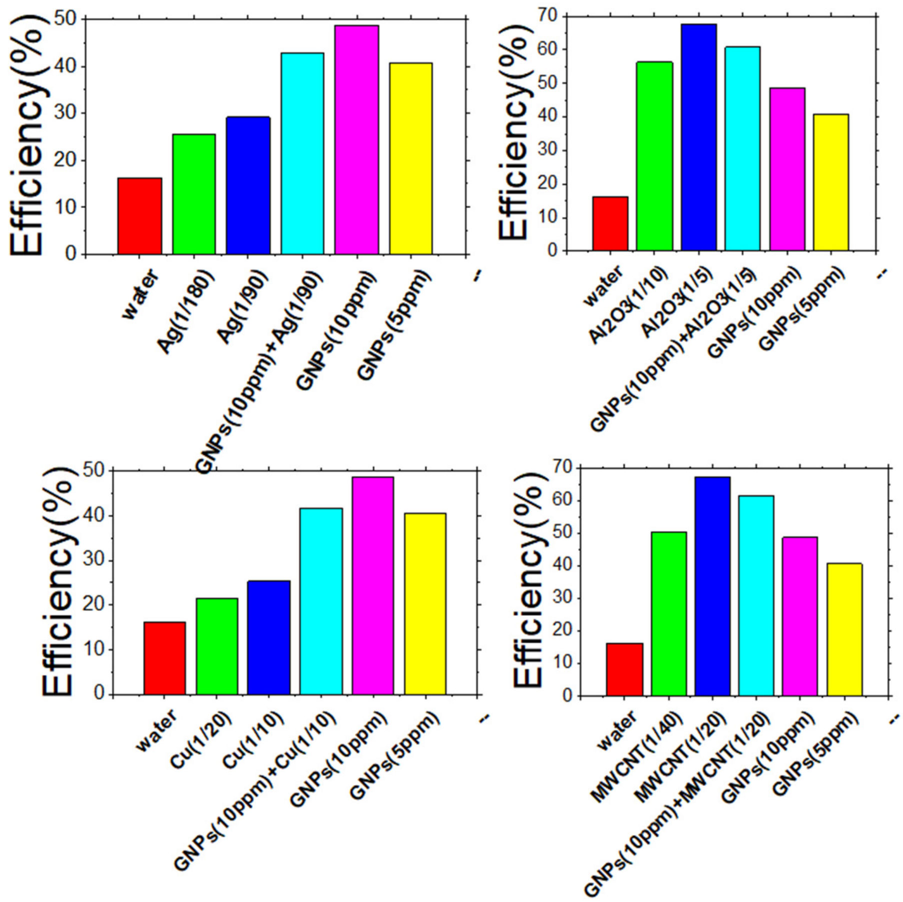

Figure 14. Absorption efficiency of experimental sample mixed with gold.

It is also found that when two different nanofluids are dispersed with each other at the same volume concentration, the mixed fluid has two peaks that are exactly the same as the mixed component, and the absorption curve is flatter than that of a single type of nanofluid. This is related to Beer's law. Because the particle size is much smaller than the wavelength of the incident light, it is reasonable to infer that the nanoparticles in the low concentration nanofluid scatter sunlight alone. The absorption line of the full spectrum of the UV–Vis–NIR spectrophotometer must pass through the intersection of two separate absorption lines. Therefore, two absorption peaks appeared in Figure 12.

A total of five sets of experiments of mixed nanofluids was carried out. The comparison chart of the experimental data obtained by the data collector and the predicted result and the images collected by the infrared thermal imager during the experiment are shown in Figures 15–20.

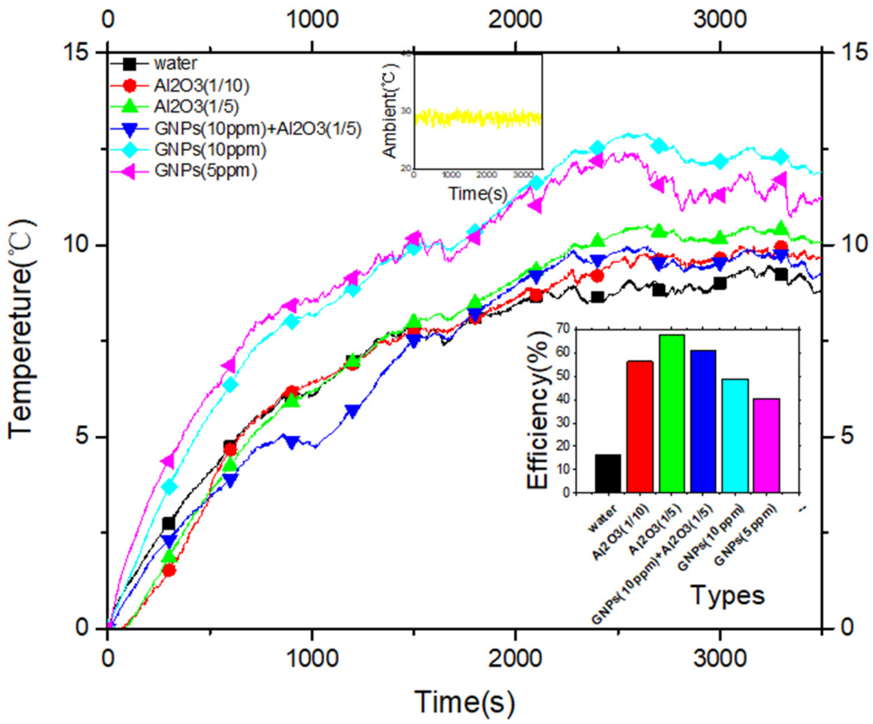

Figure 15. Predicted solar energy absorption efficiency and experimental results of Au–Cu hybrid nanofluid.

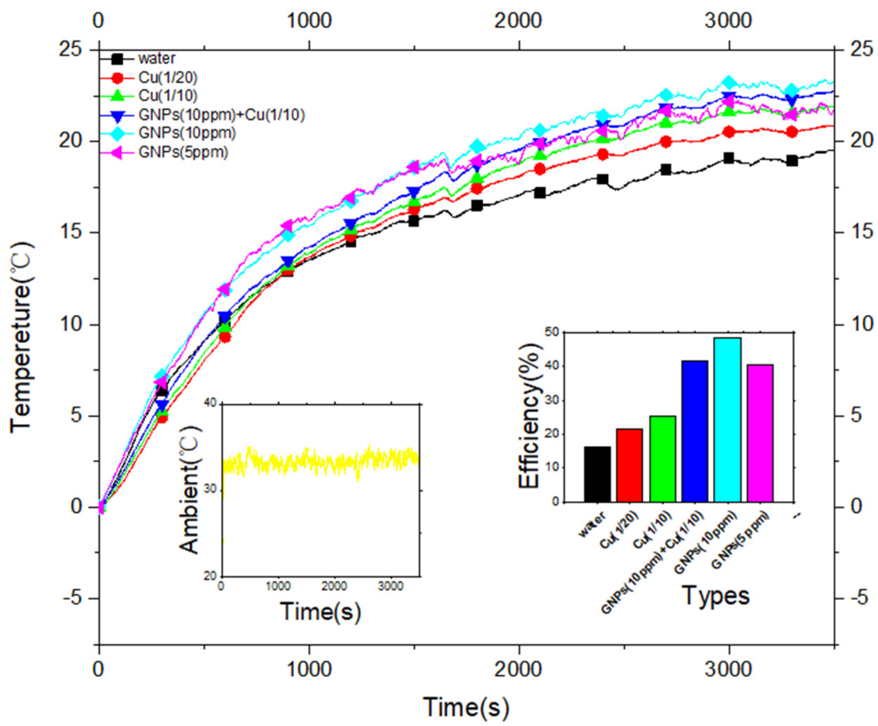

Figure 16. Predicted solar energy absorption efficiency and experimental results of Au-Al_2O_3 hybrid nanofluid.

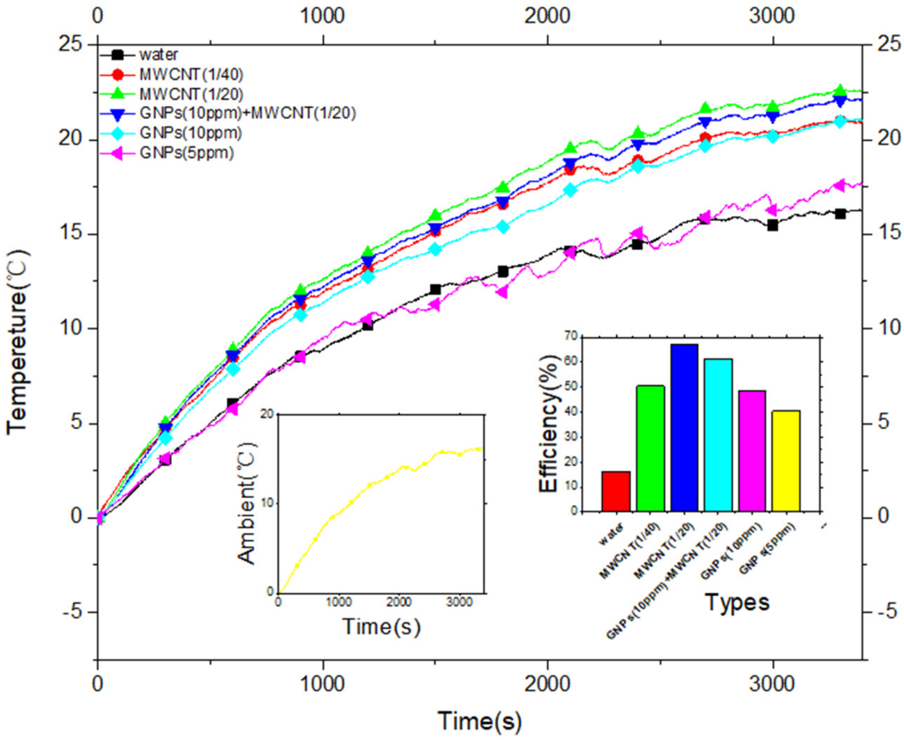

Figure 17. Predicted solar energy absorption efficiency and experimental results of Au-MWCNT hybrid nanofluid.

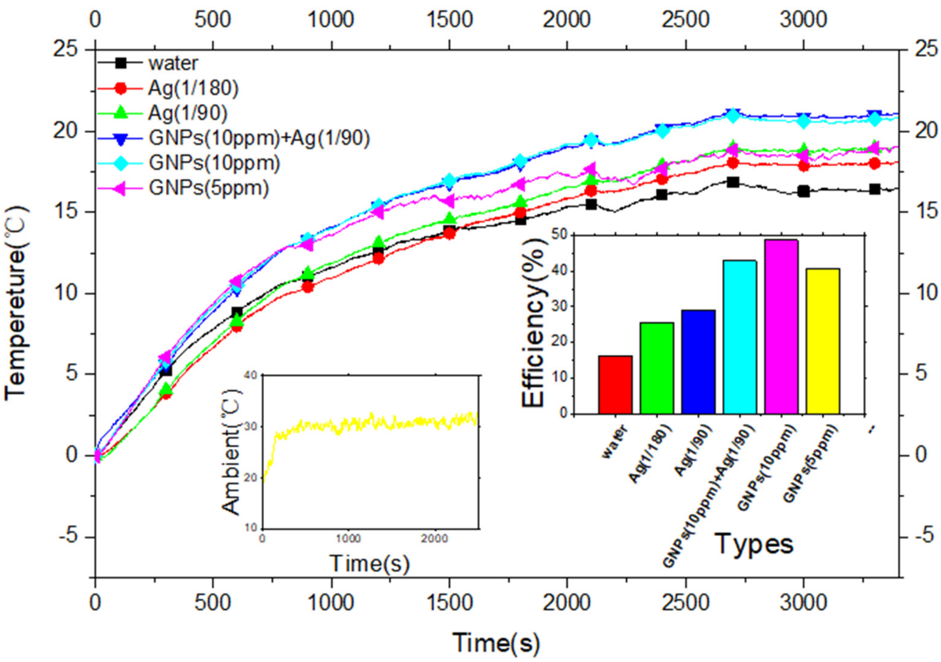

Figure 18. Predicted solar energy absorption efficiency and experimental results of Au–Ag hybrid nanofluid.

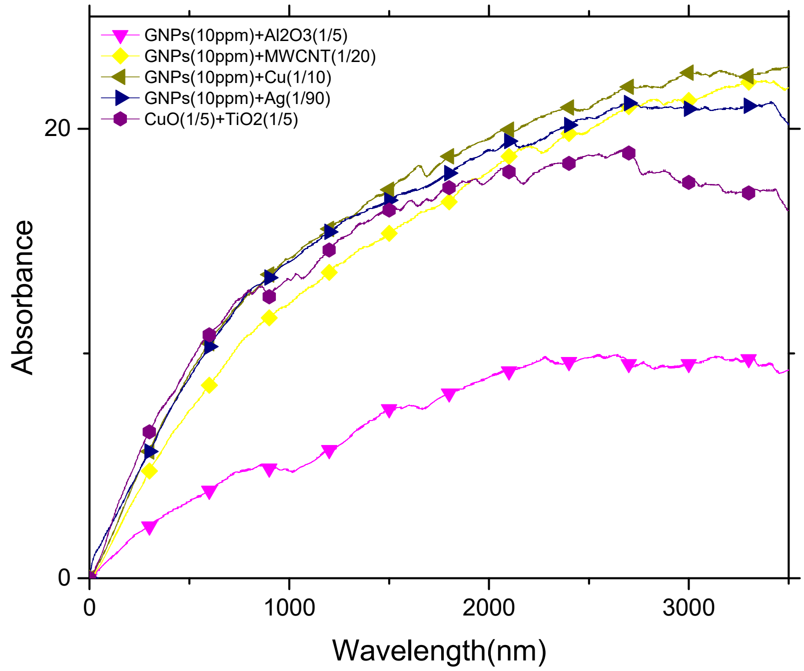

Figure 19. Predicted solar energy absorption efficiency and experimental results of Au–TiO_2 hybrid nanofluid.

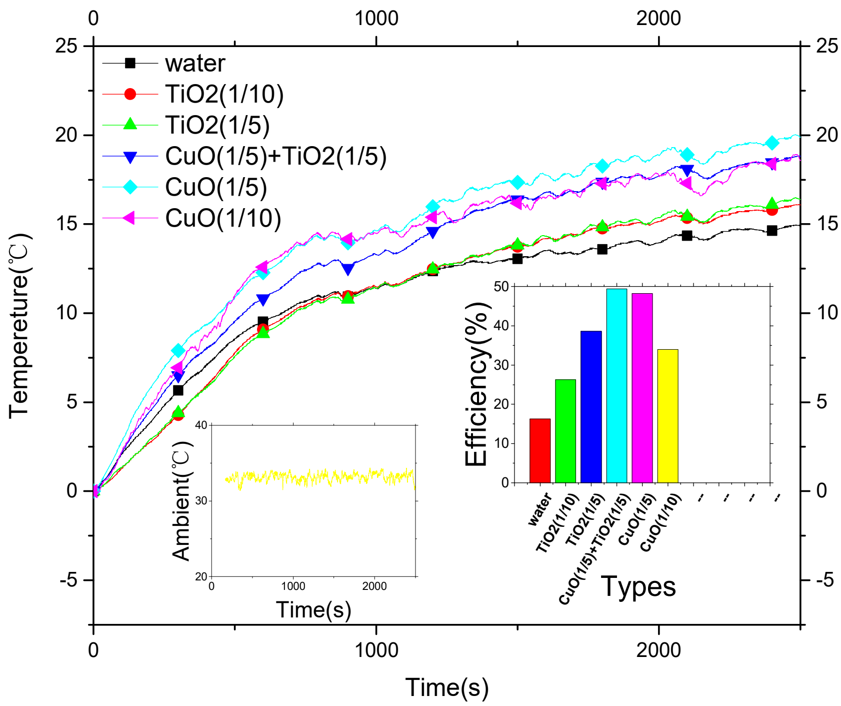

Figure 20. Experimental results of five kinds of hybrid nanofluids.

In the Au–Cu mixture experiments, the photothermal conversion efficiencies of water, 20 times diluted copper, 10 times diluted copper, mixed nanofluid of 10 ppm gold and 10 times diluted copper, 10 ppm gold nanofluid and 5 ppm gold nanofluid are calculated as 16.25%, 21.54%, 25.38%, 41.67%, 48.67%, and 40.57%, respectively. The efficiency of the mixed nanofluid of 10 ppm gold and 10 times diluted copper is lower than the absorption efficiency of 10 ppm gold nanofluid but higher than water, 20 times diluted copper, 10 times diluted copper and 5 ppm gold nanofluid.

The ambient temperature shown in Figure 15 rose from 24 °C to 30 °C in a short time, and then remained at about 30 °C. When the cooling was stopped in the experiment, the water quickly evaporated and the temperature changed rapidly. The fluctuation of the temperature curve may be caused by the failure to change the orientation of the glass tube in time, which affects the direct irradiation of the nanofluid. At about 2500 s, the ambient temperature also has a lot of fluctuations which could be attributed to the cooling of the wind. The overall experimental results are consistent with the numerical prediction results, but the photothermal conversion efficiency of the Au–Cu hybrid nanofluid is not as good as the photothermal conversion efficiency of the 10 ppm Au nanofluid. It should be related to the unsuitable concentration and proportion of the single nano–solution used in the experiment.

Although the simplification of the experimental numerical model makes the data processing simple, it may also lead to errors in the results. An error analysis of the experiment should be carried out. Environmental factors include:

(1) The temperature distribution within the glass tube;
(2) The measurement of thermocouples cannot accurately represent the average temperature of the nanofluid;
(3) A control experiment of temperature collection points should be set, and thermocouples are attached to different positions of the same glass tube for temperature measurement;
(4) The flow state of the nanofluid should be considered in the experimental setup and the completely static experimental state does not meet the actual engineering utilization conditions;
(5) The experimental operation should be more rigorous.

6. Conclusions

Due to the high light–to–heat conversion characteristics of nanofluids, direct absorption solar collectors based on nanofluids have high research value. There is a peak in the absorption curve of a single nanometer in the full spectrum, and the wavelength range of the part with a higher absorption efficiency is narrow. Simply increasing the concentration of a single nanofluid can enhance the light–to–heat conversion characteristics of the nanofluid, but for the noble metal nanomaterials with better absorption properties, the cost is relatively high, which is not conducive to engineering utilization.

In order to study the absorption characteristics of hybrid nanofluids, this paper firstly analyzes the morphology and characteristics of the nanoparticles in the nanofluid with transmission electron microscopy and scanning electron microscopy to ensure that a single nanoparticle can be observed in the hybrid nanofluid. A theoretical model of nanofluid light–to–heat conversion efficiency is proposed. The solar radiation conduction is simplified by Mie scattering theory, and a simplified model for calculating the absorption efficiency of solar radiation energy by mixed nanofluids is constructed to facilitate the evaluation of direct absorption of solar energy.

UV–Vis–NIR spectrophotometer was used to measure the solar energy absorption characteristics of the samples in all experiments, absorption curve of the nanofluids on the full spectrum are drawn, and the absorption characteristics of the nanofluids are analyzed. Multi–group control experiments were carried out on mixed nanofluid, single nanofluid, and base fluid through observing and recording the temperature change of the fluid under sunlight. Using the simplified model of the solar radiation energy absorption efficiency of the hybrid nanofluid, the absorption efficiency of the fluid in the full spectrum is calculated, and the data are analyzed in combination with the experimental results. The following conclusions could be drawn:

1. The light–to–heat conversion efficiency of nanofluids increases as the concentration increases and finally stabilizes. However, the wavelength of the absorption peak of a single nanofluid does not change with concentration.

2. The light–to–heat conversion performance of nanofluid is related to the type of nanofluid, which is slightly larger than that of the base fluid. The reason is that nanoparticles dispersed in water have strong absorption of solar energy, and the scattering effect between particles is increased. The light path of the light entering the nanofluid is conducive to the nanofluid to capture and absorb solar energy.
3. The light–to–heat conversion performance of metallic nanofluids is stronger than that of non–metallic nanofluids.
4. The mixed fluid has the same two peaks as the mixed single nanofluid, and the absorption curve is flatter than that of the single nanofluid.
5. The light–to–heat conversion characteristics of hybrid nanofluids are not necessarily stronger than that of single nanofluids. Nanoparticles with different absorption spectra need to be selected. The ratio of different concentrations and the content of different components may affect the experimental results.

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Nomenclature

A	absorbance (–)
E	spectral emissive power (W/m^3)
f_v	volume concentration (–)
L	optical depth (m)
Q	efficiency factor for Mie scattering (–)
D	particle diameter (m)
Greek symbols	
β	extinction coefficient (m^{-1})
η	efficiency (–)
λ	wavelength of light in vacuum (m)
Subscripts	
λ	wavelength related
abs	absorption
bb	black body

References

1. Choi, S.U.S.; Eastman, J.A. *Enhancing Thermal Conductivity of Fluids with Nanoparticles*; ASME: New York, NY, USA, 1995; pp. 99–105.
2. Jin, H.; Lin, G.; Bai, L.; Zeiny, A.; Wen, D. Steam generation in a nanoparticle-based solar receiver. *Nano Energy* **2016**, *28*, 397–406. [CrossRef]
3. Jin, H.; Lin, G.; Bai, L.; Amjad, M.; Filho, E.P.B.; Wen, D. Photothermal conversion efficiency of nanofluids: An experimental and numerical study. *Sol. Energy* **2016**, *139*, 278–289. [CrossRef]
4. Jin, H.; Lin, G.; Zeiny, A.; Bai, L.; Wen, D. Nanoparticle-based solar vapor generation: An experimental and numerical study. *Energy* **2019**, *178*, 447–459. [CrossRef]
5. Khullar, V.; Tyagi, H.; Hordy, N.; Otanicar, T.P.; Hewakuruppu, Y.; Modi, P.; Taylor, R.A. Harvesting solar thermal energy through nanofluid-based volumetric absorption systems. *Int. J. Heat Mass Transf.* **2014**, *77*, 377–384. [CrossRef]
6. Ishii, S.; Sugavaneshwar, R.P.; Nagao, T. Titanium Nitride Nanoparticles as Plasmonic Solar Heat Transducers. *J. Phys. Chem. C* **2016**, *120*, 2343–2348. [CrossRef]
7. Zhou, L.; Tan, Y.; Ji, D.; Zhu, B.; Zhang, P.; Xu, J.; Gan, Q.; Yu, Z.; Zhu, J. Self-assembly of highly efficient, broadband plasmonic absorbers for solar steam generation. *Sci. Adv.* **2016**, *2*, e1501227. [CrossRef]
8. Yeshchenko, O.A.; Kutsevol, N.V.; Naumenko, A.P. Light-Induced Heating of Gold Nanoparticles in Colloidal Solution: Dependence on Detuning from Surface Plasmon Resonance. *Plasmonics* **2015**, *11*, 345–350. [CrossRef]
9. Tullius, T.; Bayazitoglu, Y. Temperature of a metallic nanoparticle embedded in a phase change media exposed to radiation. *Int. J. Heat Mass Transf.* **2016**, *93*, 980–990. [CrossRef]

10. Otanicar, T.P.; Phelan, P.E.; Prasher, R.S.; Rosengarten, G.; Taylor, R.A. Nanofluid-based direct absorption solar collector. *J. Renew. Sustain. Energy* **2010**, *2*, 033102. [CrossRef]
11. Amjad, M.; Jin, H.; Du, X.; Wen, D. Experimental photothermal performance of nanofluids under concentrated solar flux. *Sol. Energy Mater. Sol. Cells* **2018**, *182*, 255–262. [CrossRef]
12. Jin, H.; Lin, G.; Guo, Y.; Bai, L.; Wen, D. Nanoparticles enabled pump-free direct absorption solar collectors. *Renew. Energy* **2019**, *145*, 2337–2344. [CrossRef]
13. Jin, H.; Lin, G.; Zeiny, A.; Bai, L.; Cai, J.; Wen, D. Experimental study of transparent oscillating heat pipes filled with solar absorptive nanofluids. *Int. J. Heat Mass Transf.* **2019**, *139*, 789–801. [CrossRef]
14. Zeiny, A.; Jin, H.; Bai, L.; Lin, G.; Wen, D. A comparative study of direct absorption nanofluids for solar thermal applications. *Sol. Energy* **2018**, *161*, 74–82. [CrossRef]
15. Zeiny, A.; Jin, H.; Lin, G.; Song, P.; Wen, D. Solar evaporation via nanofluids: A comparative study. *Renew. Energy* **2018**, *122*, 443–454. [CrossRef]
16. Karami, M.; Bahabadi, M.A.; Delfani, S.; Ghozatloo, A. A new application of carbon nanotubes nanofluid as working fluid of low-temperature direct absorption solar collector. *Sol. Energy Mater. Sol. Cells* **2014**, *121*, 114–118. [CrossRef]
17. Chen, M.; He, Y.; Zhu, J.; Kim, D.R. Enhancement of photo-thermal conversion using gold nanofluids with different particle sizes. *Energy Convers. Manag.* **2016**, *112*, 21–30. [CrossRef]
18. Chen, M.; He, Y.; Zhu, J.; Shuai, Y.; Jiang, B.; Huang, Y. An experimental investigation on sunlight absorption characteristics of silver nanofluids. *Sol. Energy* **2015**, *115*, 85–94. [CrossRef]
19. Chen, M.; He, Y.; Zhu, J.; Wen, D. Investigating the collector efficiency of silver nanofluids based direct absorption solar collectors. *Appl. Energy* **2016**, *181*, 65–74. [CrossRef]
20. Noor, F.; Vorozhtsov, A.; Lerner, M.; Filho, E.P.B.; Wen, D. Thermal-Chemical Characteristics of Al–Cu Alloy Nanoparticles. *J. Phys. Chem. C* **2015**, *119*, 14001–14009. [CrossRef]
21. He, Y.; Wang, T.; Deen, N.G.; Annaland, M.V.S.; Kuipers, H.; Wen, D. Discrete particle modeling of granular temperature distribution in a bubbling fluidized bed. *Particuology* **2012**, *10*, 428–437. [CrossRef]
22. Khullar, V.; Tyagi, H.; Phelan, P.; Otanicar, T.; Singh, H.; Taylor, R.A. Solar Energy Harvesting Using Nanofluids-Based Concentrating Solar Collector. *J. Nanotechnol. Eng. Med.* **2012**, *3*, 031003. [CrossRef]
23. Zhang, H.; Chen, H.-J.; Du, X.; Lin, G.; Wen, D. Dependence of Photothermal Conversion Characteristics on Different Nanoparticle Dispersions. *J. Nanosci. Nanotechnol.* **2015**, *15*, 3055–3060. [CrossRef] [PubMed]
24. Jin, X.; Lin, G.; Zeiny, A.; Jin, H.; Bai, L.; Wen, D. Solar photothermal conversion characteristics of hybrid nanofluids: An experimental and numerical study. *Renew. Energy* **2019**, *141*, 937–949. [CrossRef]