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Broad-band absorption and photo-thermal conversion properties of zirconium carbide aqueous nanofluids

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ABSTRACT

Broad-band absorbers are very important for solar thermal utilization. However, seeking ideal solar absorbers whose absorption spectra match well with the solar spectrum is still a great challenge. In this work, zirconium carbide (ZrC) nanofluids with broad-band absorption characteristic were prepared by milling and dispersing ZrC nanoparticles in water. The ZrC nanoparticles show strong optical absorption in the range from 300 to 2000 nm. At a penetration distance of 1 cm, the ZrC nanofluids of 0.02 wt% can absorb almost 100% of the solar irradiation in the full spectrum and the solar weighted absorption coefficient (A_m) is 0.99. The results indicate that the ZrC nanofluids of 0.02 wt% are very close to the ideal solar irradiation absorbers. The photo-thermal conversion efficiency of the ZrC nanofluids was evaluated by a direct method focusing on the nanofluids themselves instead of indirectly represented by the efficiency of the solar thermal collector as presented in the previous reports. By recording and analyzing the temperature rise of the nanofluids under the illumination of a solar simulator, the photo-thermal conversion efficiency for the ZrC nanofluids of 0.02 wt% was determined to be 92%. The high efficiency is attributed to the broad-band absorption of the ZrC nanoparticles.

1. Introduction

Solar energy becomes extremely significant for global ecological integrity and sustainable development because of energy crisis and environmental pollution. Recently, nanofluids, a new working fluid containing nano-sized particles [1,2], have been found to be very promising for the photo-thermal utilization of solar energy [3]. Nanofluids can absorb light and generate heat because of their photo-thermal conversion (PTC) properties. The optical absorption properties of nanofluids have the most significant effect on the PTC properties. Therefore, great research effort has been made to study the optical properties of various nanofluids containing nonmetallic, metallic and hybrid nanoparticles. Based on their optical behaviors, nanofluids can be classified into two categories: nanofluids having excellent absorption in the visible light region [4–18] and those having excellent absorption in the infrared region [19–22]. Our research group prepared CNTs glycol nanofluids and found that small amount of CNTs resulted in significant enhancement in the absorption of visible light [4]. Phelan and co-workers reported that nanofluids containing aluminum, copper, graphite, and silver nanoparticles have high extinction coefficient in visible light region [5]. Ag@TiO_2 core@shell structures and the corresponding nanofluids were found to have strong absorption in the visible light region [6,7]. The optical absorption properties of gold nanoparticles were studied and the absorption peak is typically located at around 520–580 nm [8–10]. Many nanofluids containing carbon materials such as carbon nanohorns [11,12], carbon black [13], and graphene [14] have excellent absorption in the visible light region. Some nanofluids containing metal materials (Cu [15], Ag [16]) and inorganic nonmetallic materials (CuO [17], Al_2O_3 [18]) also have good absorption in the visible light region. On the other hand, some nanofluids containing semiconductor materials often have absorption in the near infrared (NIR) region. Wang et al. studied nanofluids containing plasmonic copper sulfide nanocrystals and found high extinction coefficients in the NIR region [19]. Tian et al. reported that the aqueous dispersion of Cu_9S_5 nanocrystals exhibited strong absorption at 980 nm [20]. The ultrathin PEGylated $W_{18}O_{49}$ nanowires [21] and the hydrophilic molybdenum oxide nanomaterials [22] were also found to have high absorbance at 980 nm. The above-mentioned nanofluids often exhibit excellent absorption in either visible light region (400–780 nm) or NIR region (780–2500 nm). However, they seldom show excellent absorption in both regions simultaneously. On the other hand, the portion of solar radiation energy in the visible light region adds up to

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Nomenclature

λ	wave length (nm)
$A_m(x)$	solar weighted absorption coefficient at a given penetration distance
$\alpha(\lambda)$	transmittance per unit wavelength
$S_m(\lambda)$	incident solar irradiance at a given wavelength (W/m^2)
x	penetration distance (cm)
ΔT	temperature rise (°C)
T	temperature (°C)
t	time (s)
m_i	mass of component (kg)
c_i	specific heat capacity of component (J/(kg·K))
Q_{in}	the heat input from photo-thermal conversion (J/s)
Q_{dis}	the heat dissipation (J/s)
A	area exposed to solar illumination (m^2),
S_m	integral incident solar irradiance of full spectrum (W/m^2)
η	photo-thermal conversion efficiency
A_{dis}	surface area of heat dissipation (m^2)
$T(t)$	temperature of the nanofluids at time t (°C)
T_{am}	the ambient temperature (°C)
T_{eq}	the equilibrium temperatures (°C)
B	constant rate of heat dissipation (s^{-1})
m_w	mass of water (kg)
c_w	specific heat capacity of water (J/(kg·K))
A_m	Solar weighted absorption coefficient
h	heat transfer coefficient ($W/(m^2 \cdot K)$)

50%, while that in the NIR region is about 45% [23]. Therefore, it is important to prepare nanofluids with excellent light absorption in both visible light region and NIR region in order to get high PTC performance in a wide spectral region.

Besides the optical absorption properties, the PTC efficiency is another important parameter to evaluate the PTC performance of the nanofluids. Unfortunately, reliable methods to evaluate the PTC efficiency of nanofluids have not been well developed. In the literatures, the efficiencies of solar collectors or solar water heaters are often applied to represent the PTC efficiency of the nanofluids used as working fluids. However, some experimental factors other than nanofluids themselves may also have great influence on the efficiency of the solar collector. Many researches show that the mass flow rate of the working fluid is a very sensitive impact factor on the efficiency of the solar collector [24–28]. These researches indicate that present evaluation methods focus on the efficiencies of the solar collecting systems instead of the efficiencies of the nanofluids themselves. It may cause remarkable discrepancy because the efficiency of the solar collector can be impacted by many parameters [29–33]. In a direct absorption solar collector, the heat generated from the photo-thermal conversion effect of the nanofluids goes in two ways: the first part increases the temperature of the fluids and the second part transfers to the facility and subsequently the environment [34]. In many works, only the first part was considered [35–37], and thus the calculated efficiency was lower than the true photo-thermal conversion efficiency of the nanofluids. If the facility is well insulated, the efficiency may increases significantly. From a practical point of view, the total efficiency of the facility is very important. However, the same nanofluid can give different thermal efficiencies on different collectors, leading to significant discrepancy. Therefore, we aimed to compare the photo-thermal conversion properties of the nanofluids by focusing on the nanofluids themselves. In our opinion, it is reasonable that the photo-thermal conversion efficiency of the nanofluids is higher than the total efficiency.

In the current work, zirconium carbide (ZrC) aqueous nanofluids were prepared and studied as broad-band solar irradiation absorbers. It was demonstrated that the ZrC nanofluids were very close to the ideal solar irradiation absorbers and the PTC properties of the nanofluids can be significantly enhanced due to the broad-band absorption. We then used a modified method to directly evaluate the PTC efficiency of the nanofluids based on the equilibrium between the heat generation and the heat dissipation of the nanofluids. This method focuses on the nanofluids themselves instead of the solar thermal collectors and thus can give more reasonable evaluation on the PTC performance of the nanofluids.

2. Experiment section

2.1. The preparation of the ZrC nanofluids

In this work, nanofluids were prepared by a two-step method. In a typical procedure, 50 g of ZrC nanopowders (supplied by Shanghai Chaowei Nanotechnology Co., Ltd.), together with 5 g of Polyvinylpyrrolidone (PVP) as dispersant, were added to 200 mL of deionized water and then milled in a laboratory attritor (Qingdao Union Process Precision Machinery Co., Ltd.) for 8 h to get a concentrated suspension. ZrC nanofluids of different mass fractions were prepared by diluting the suspension with deionized water under ultrasonic oscillation.

2.2. Characterization of the ZrC nanofluids

ZrC nanoparticles were separated from the nanofluids and dried before their X-ray diffraction (XRD) pattern was recorded on a Rigaku D/Max r-A diffractometer. Transmission electron microscope (TEM, JEM-1200EX) was applied to investigate the size and shape of the nanoparticles. The size distribution of ZrC nanoparticles was tested using a Malvern zetasizer Nano-ZS90. The absorption spectrum of the ZrC nanoparticles was measured from 350 to 2000 nm on a U-4100 UV/Vis/NIR spectrophotometer (photometric accuracy: ±0.002 Abs (0–0.5 Abs), ±0.004 Abs (0.5–1.0 Abs)). The transmission spectra of the nanofluids were measured using a Lambda900 spectrophotometer (stray light $\leq$ 0.00007%T, photometric accuracy: ±0.0003 Abs), where the nanofluid samples were held in quartz cuvettes with 1 cm beam path length.

2.3. Evaluation of the PTC properties of the ZrC nanofluids

A lab-made evaluating system was used to characterize the PTC properties of the ZrC nanofluids. A schematic diagram of the system is presented as Fig. 1. The system is equipped with a xenon lamp working as a solar simulator. The power of the xenon lamp was adjusted and the irradiance arrived at the nanofluids was set to be 1020 W/m^2, which was indicated on spot by a TBQ-2 pyranometer (Jinzhou Sunshine Meteorological Science and Technology Co., Ltd., the test scope 0–2000 W/m^2; stability ±2%). In a typical testing procedure, 4 mL of nanofluids was sealed in a quartz cuvette with internal dimensions of 4 cm × 1 cm × 1 cm. The cuvette was then inserted into a polystyrene foam working as insulation. Only one direction of the cuvette was exposed and the exposed surface area of the nanofluids was 4 cm^2. A thermocouple with an accuracy of ±0.1 °C was fixed in the nanofluid to record the temperature. The temperature in the nanofluid was allowed to reach equilibrium at ambient temperature before the testing began. Then, the xenon lamp was turned on and the temperature in the nanofluid gradually increased before reaching an equilibrium temperature. The xenon lamp was turned off after the nanofluid was kept at the equilibrium temperature for a period of time and