



Research Paper

Solidification behavior of hybrid TiO₂ nanofluids containing nanotubes and nanoplatelets for cold thermal energy storage



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HIGHLIGHTS

- Hybrid TiO₂ nanofluids reduce subcooling degree through improved dispersion stability.
- These nanofluids shorten freezing time through enhanced thermal conductivity.
- These nanofluids improve solidification performance.

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ABSTRACT

The solidification behavior of hybrid nanofluids containing TiO₂ nanotubes (TiNTs) and nanoplatelets (TiNPs) was investigated in 10 freeze–melt cycles and the results were compared with those of individual TiNT and TiNP nanofluids. Hybrid TiO₂ nanofluids showed lower supercooling degrees because of larger surface area exposed to water, and shorter freezing time as a result of higher thermal conductivities, compared with individual TiNT and TiNP nanofluids. A maximum reduction of 5.27 ± 0.2 °C in supercooling degree and 56.42% in freezing time were achieved for hybrid nanofluids containing 25% and 50% TiNPs, respectively. The supercooling degree and freezing time of hybrid nanofluids showed less of an increase across 10 freeze–melt cycles as they have better dispersion stability compared with individual nanofluids. Evidently, the smallest increase of 0.68 ± 0.2 °C in supercooling degree and 29.85% in freezing time was achieved in 0.1 wt.% hybrid nanofluid compared with 2.02 ± 0.2 °C and 130.37% for individual TiNT nanofluids and 3.98 ± 0.2 °C and 101.08% for individual TiNP nanofluids. These promising performances highlight the outstanding thermal energy storage applications of hybrid nanofluids.

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1. Introduction

Energy conservation and highly-efficient utilization are primary concerns in the field of energy production. Cold thermal energy storage has become one of the widely applied solutions to the electrical power imbalance between daytime need and nighttime abundance because it can overcome or mitigate the time gap between energy supply and energy usage. Latent heat storage during solidification–melt process of phase change materials (PCMs) has been identified as an efficient storage technique for thermal energy because of its high storage density, low cost, and small temperature span [1,2]. It shows wide applications and bright pro-

spects in many fields such as air conditioning systems and refrigeration, industrial cooling, and so on.

Water has been proven to be one of the major PCM categories applied in cold thermal energy storage systems because of its large latent heat, abundance of source, chemical compatibility, superior storage density, and environmentally friendly properties [1,2]. However, the relatively large supercooling degree and low thermal conductivity of water are two important weaknesses to overcome. Supercooling behavior is undesirable in cold thermal energy storage systems. A high degree of supercooling leads to slow nucleation rate and growth rate of crystal nuclei, which requires long freezing time [2,3]. This condition also reduces the energy storage retrieval rate and refrigeration efficiency and cannot effectively enhance the performance of energy storage devices [5]. Therefore, efforts are necessary to reduce or even eliminate the supercooling degree of water as much as possible in thermal energy storage applications.

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Nomenclature

BS	back scattering light intensity
ΔBS	back scattering light intensity change
$c_{p(T)}$	specific heat, J/(kg K)
$k_{(T)}$	thermal conductivity, W/(m K)
ΔG	surface free energy, J/m ²
ΔH	latent heat, kJ/kg
T	Temperature, °C
ΔT	supercooling degree, °C
t	Time, s

Greek letters

$\alpha_{(T)}$	thermal diffusion coefficient, m ² /s
$\rho_{(T)}$	density, kg/m ³

Abbreviations

D	dimensional
PCM	phase change material
TiNTs	TiO ₂ nanotubes
TiNPs	TiO ₂ nanoplatelets
TEM	transmission electron microscopy
TSI	Turbiscan Stability Index

Subscripts

f	freezing
n	nucleation
p	phase change

With the development of nanotechnology, nanofluid, a novel-type of heat transfer fluid, has been proposed. Nanofluid is prepared by dispersing solid nanoparticles of high thermal conductivities in conventional working fluids and is a promising candidate of PCMs for cold thermal energy storage [6–8]. The previous study indicated that nanoparticles suspended in nanofluids could act as nucleation agents to promote heterogeneous nucleation of water. Therefore, nanofluids undergo a lower degree of supercooling in the solidification process compared with water alone. In the literature, the solidification performance of nanofluids with addition of various metallic, metal oxide, and carbon nanoparticles has been characterized. A large number of experiments have shown that nanofluids could be applied as PCMs because nanoparticle additives could enhance thermal conductivity, promote heterogeneous nucleation, shorten phase transition time, and reduce supercooling of water [7–21]. For instance, Chopkar et al. prepared nanofluids by dispersing approximately 0.2–2.0 vol.% nanocrystalline Al₇₀Cu₃₀ particles in ethylene glycol; a dramatic thermal conductivity enhancement of over 200% with merely 1.5 vol.% particles present in the liquid is reported; the conductivity ratio increases further with a greater amount of particles if not for concerns regarding stability [4]. Li et al. prepared nanofluids by dispersing platelet-like and ultrathin graphene in water and studied the solidification behavior of nanofluids; they reported that graphene is a highly effective additive in promoting heterogeneous nucleation because it can eliminate the supercooling degree of water with addition of only 0.02 wt.% graphene owing to its ultrahigh specific surface area, and the phase transition time can be shortened by 23.33% because of enhanced thermal conductivities [19].

The previous study mainly focused on factors that influence the solidification behavior of nanofluids, including hydrophilic and hydrophobic property of nano-additives [6], concentration and specific surface area of nanoparticles [15,18], and effect of dispersant addition [17,18]. Generally, nano-additives with larger specific surface area and hydrophilic property are more suitable for promoting heterogeneous nucleation of water as larger surface areas exposed to water can provide more nucleation sites and increase the probability of nucleation [18]. Likewise, dimensionality of nanoparticles is also a significant factor. Nano-additives with different dimensionalities possess different crystallization behaviors. For instance, in isothermal studies of high-density polyethylene (HDPE) containing 0D, 1D, and 2D carbon nanofillers, the isothermal crystallization rate became slower with the addition of lower-dimensional carbon nanofillers, and the isothermal crystallization incubation time of HDPE lengthened [22]. Nofar et al. studied the effects of nano-sized and micro-sized additives (micro-sized talc, nanosilica, and nanoclay) with different sizes

and aspect ratios on the crystallization kinetics of polylactide (PLA) and PLA/CO₂ mixtures; they reported that the micro-sized talc particles enhanced the crystallization rate of the PLA and the nanoclay with long-aspect ratio delayed the initial crystal growth [23]. The effects of both 1D and 2D high aspect-ratio carbon nano-additives on non-isothermal crystallization of aqueous nanofluids have been investigated recently [24]; the findings showed that the 2D graphene nanoplatelets (GNPs) induced a supercooling degree that was generally lower than that for 1D carbon nanotubes (CNT)-based nanofluids as a result of the large contact area of the 2D GNPs. However, the larger size of GNPs could hinder crystal growth during late phase of crystallization, thereby leading to an increase in half crystallization time. The question that needs investigation is whether collaboration of TiNTs and TiNPs occur, which leads to better solidification behaviors in both supercooling degree and freezing time for promising performance of cold thermal energy storage.

Dispersion stability of nanofluids is also a key factor in maintaining durability and reliability of cold thermal energy storage properties. However, the stability of nanofluids applied as PCMs is rarely studied. Generally, nanofluids with better dispersion stability show more stable thermal performance; thus, their application as PCMs is more promising. Previous studies have indicated that platelet-like nanoparticles with 2D structure can conduct effective steric hindrance for spherical or tube nanoparticles; thus, the aggregation will also be reduced and the stability of nanofluids will be improved [25,26]. More importantly, the reduced aggregation of nanoparticles resulted in a decrease in surface area reduction of nanoparticles exposed to water and is favorable for heterogeneous nucleation of water [14,17,21]. Our previous study has reported that the stability of TiO₂-H₂O nanofluids can be effectively improved by mixing two differently-shaped hydrophilic TiNTs and TiNPs with appropriate concentration ratios [27,28]. The improved dispersion of TiNTs and TiNPs offer more nucleation sites and increased the possibility of nucleation. Therefore, comparing the solidification behaviors of both hybrid nanofluids containing 1D TiNTs and 2D TiNPs and individual nanofluids is necessary to demonstrate whether hybrid TiO₂ nanofluids have better solidification characteristics than individual TiNT and TiNP nanofluids.

2. Materials and methods

2.1. Synthesis of TiNTs and TiNPs

The TiNTs and TiNPs were synthesized by hydrothermal method using commercially available reagents [29,30]. All of the reagents were used as received without further purification. In a

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