



# Non-isothermal crystallization of aqueous nanofluids with high aspect-ratio carbon nano-additives for cold thermal energy storage



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## HIGHLIGHTS

- Aqueous nanofluids with CNTs or GNPs were prepared for cold thermal energy storage.
- Non-isothermal crystallization of the aqueous nanofluids was tested by DSC method.
- The supercooling degree reduces due to the nucleating effect of the nanoparticles.
- GNPs in general lead to greater drops of latent heat of crystallization than CNTs.
- The crystallization rates were shown to vary by crystallization kinetics analysis.

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## ABSTRACT

Non-isothermal crystallization of aqueous nanofluids in the presence of two types of high aspect-ratio carbon nano-additives, i.e., carbon nanotubes (CNTs) and graphene nanoplatelets (GNPs), was characterized by means of differential scanning calorimetry (DSC). A parametric investigation was performed on various concentrations of the nanofluids as well as various cooling rates during the DSC tests. In addition to the supercooling degree and latent heat of crystallization, the crystallization kinetics was also analyzed by both the Ozawa method and a modified Ozawa-based method. It was shown that dilute loading of CNTs or GNPs leads to reduction of the supercooling degree up to 5 °C due to the nucleating effect. The planarly-shaped GNPs featuring large contact area perform better than CNTs in facilitating heterogeneous nucleation, which greatly suppress crystal growth during the late phase of non-isothermal crystallization. In contrast to the case of GNPs, CNTs may be able to accelerate crystallization up to nearly 37% at relatively dilute loadings, especially when the cooling rate is low. The CNT-based aqueous nanofluids exhibit more balanced performance in supercooling degree, latent heat of crystallization, and crystallization kinetics, which may be utilized as an emerging candidate of phase change materials for cold thermal energy storage.

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## 1. Introduction

Thermal energy storage (TES) units have been extensively incorporated into man-made energy conversion and utilization systems, e.g., solar thermal power, water heaters, and buildings, etc., in an effort to improve the thermal efficiency. Latent heat storage during solid–liquid transitions of phase change materials

(PCMs) has been identified as an efficient approach to TES due to the high storage density, small temperature span, low cost, and so on. Thermal energy of low to high grades, as classified by the temperature, may be stored by latent heat TES by carefully choosing the PCMs with appropriate phase change temperatures. Water, a ubiquitous matter on the earth, has long been practiced in cold TES [1] for its abundance, chemical compatibility, and superior storage density with application to food preservation and air conditioning [2].

The relatively low thermal conductivity of water and other common low-temperature PCMs, such as hydrated salts and paraffin, however, is one of the most important shortcomings to be overcome

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## Nomenclature

$a$	exponent, –
$c$	concentration, wt.%
$F$	cooling rate constant, $^{\circ}\text{C}/\text{min}^{1-a}$
$H$	enthalpy of crystallization, kJ/kg
$K$	crystallization rate constant, $(^{\circ}\text{C}/\text{min})^m$
$m$	Ozawa constant, –
$t$	time, min
$T$	temperature, $^{\circ}\text{C}$
$X$	relative crystallinity, –

### Greek symbol

$\phi$	cooling rate, $^{\circ}\text{C}/\text{min}$
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### Subscripts

0	baseline case
1/2	half crystallization
c	crystallization
m	melting
sc	supercooling
t	time
T	temperature

to improve the energy storage/retrieval rates [3]. Nanofluids, engineered by dispersing highly-conductive nanoparticles into conventional working fluids, have thus found an extended functionality to be an emerging candidate of composite PCMs for TES with enhanced effective thermal conductivity [4]. In addition to the thermal conductivity enhancement, TES performance, i.e., melting/solidification behaviors, of aqueous nanofluids has also been studied [5,6].

Carbon nanoparticles have attracted increasing attention to serve as the fillers for composite PCMs due to their high thermal conductivity and low density [4]. The early efforts on this subject have focused on one-dimensional (1-D) carbon nanomaterials from carbon/graphite nanofibers [7–9] to carbon nanotubes (CNTs) [9–14]. The emerging family of two-dimensional (2-D) carbon nanomaterials, i.e., monolayer graphene and multi-layered graphene/graphite nanoplatelets (GNPs), have recently stood out due to the exceptional thermal properties as compared to their 1-D counterparts [14–26]. Both 1-D and 2-D carbon nanomaterials possess a high aspect ratio that is partially responsible for their superior size-related performance.

Other than the low thermal conductivity, significant supercooling during freezing of water has been identified as another important shortcoming that degrades its cold TES performance. The involvement of minute additives that serve as nuclei during ice formation (crystallization) has proved to be able to reduce the supercooling degree of water. Therefore, the presence of nanoparticles may also be able to perform as nuclei in addition to their primary functionality of enhancing the thermal conductivity of nanofluids. In the literature, the freezing point (supercooling degree), latent heat of crystallization, and crystallization kinetics of aqueous nanofluids have been characterized, both isothermally and non-isothermally, for a variety of metallic, metal oxide, and high aspect-ratio carbon nano-additives [27–38].

The crystallization behaviors of nanocomposite polymers with carbon nanofillers have shown to be rely on the dimensionality of the fillers [39]. There is, however, a lack of direct comparison of the performance among the high aspect-ratio carbon nano-additives for aqueous nanofluids, although the effects of graphene and graphene oxide additives on the supercooling degree have been investigated recently by means of isothermal crystallization [37,38]. In order to extend the existing knowledge, this study aims at investigating the effects of both 1-D and 2-D high aspect-ratio carbon nano-additives on non-isothermal crystallization of aqueous nanofluids.

## 2. Experimental

### 2.1. Preparation and characterization of the aqueous nanofluids

In this study, multi-walled CNTs and GNPs consisting of a number of layers of monolayer graphene, both supplied by Chengdu

Organic Chemicals Co. Ltd., were utilized as the representative 1-D and 2-D high aspect-ratio carbon nano-additives, respectively. The specified size and aspect ratio of the two-types of carbon nano-additives adopted are listed in Table 1. Preparation of the aqueous nanofluids follows the widely-adopted two-step protocol by first dispersing the pristine carbon nanoparticles, in the form of black powders, into deionized water at amounts leading to desired concentrations, then followed by stirring and intensive sonication by 10 min each. A total number of 5 dilute concentrations ( $c$ ) by weight, i.e.,  $c = 0.1, 0.5, 1, 2,$  and  $4$  wt.%, of both CNT- and GNP-based aqueous nanofluids were prepared along with pure water as the baseline case ( $c = 0$  wt.%) for comparison. The nanofluids were prepared in the absence of any surfactants in order not to interfere the crystallization tests, although the use of surfactants is often required for stability concern.

The high aspect-ratio carbon nano-additives after dispersion were characterized visually by transmission electron microscopy (TEM), as illustrated in Fig. 1a and b. The observed dimensions of the CNTs and GNPs are in fairly good agreement with those specified by the supplier (see Table 1), although both the length of CNTs and the thickness of GNPs are not able to be identified directly from Fig. 1. The GNPs are in the form of wrinkled thin films with the small thickness being well verified by the transparency, as exhibited in Fig. 1b. Even without any surfactants, good dispersion of the carbon nano-additives was achieved. The CNT- and GNP-based aqueous nanofluids are of acceptable stability without visible precipitation (see Fig. 1c and d) up to 1 h that was long enough to finish the tests, although both CNTs and GNPs are hydrophobic in nature. As shown in Fig. 1e and f, after being placed on the shelf for 24 h, sedimentation to the bottom of the jars are clearly observed for GNP-based nanofluids, although the CNT-based nanofluids appear to be still stable.

### 2.2. Non-isothermal crystallization of the aqueous nanofluids

Non-isothermal crystallization of the nanofluids was tested on a differential scanning calorimeter (DSC) under nitrogen atmosphere. A specimen of about  $10 \mu\text{L}$  was used in all measurements. The DSC tests were carried out following the procedure below. A specimen was first heated from room temperature to  $30^{\circ}\text{C}$  at a ramping rate of  $5^{\circ}\text{C}/\text{min}$  and maintained at that temperature for

**Table 1**  
Specifications of the carbon nano-additives adopted.

Material	Size	Aspect ratio	Purity (wt.%)
CNTs	Length: 10–30 $\mu\text{m}$ , diameter: 10–20 nm	500–3000	>95
GNPs	Diameter: 5–10 $\mu\text{m}$ , thickness: 4–20 nm	250–2500	>99

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