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# Ultrahigh specific surface area of graphene for eliminating subcooling of water

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## HIGHLIGHTS

- A very small amount of graphene can eliminate the subcooling degree of water.
- Graphene is more suitable than nanoparticles to eliminate subcooling of water.
- Surfactants will reduce subcooling degree and increase total freezing time.

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## ABSTRACT

Graphene is widely utilized because of its exceptional properties, such as strong mechanical strength, low weight, nearly optical transparency, and excellent conductivity of heat and electricity. In this study, we used the ultrahigh specific surface area of graphene due to its inherently two-dimensional nature to reduce the subcooling of freezing of a phase change material. The results enable graphene's application in energy storage using the latent heat of phase transition. The need for subcooling to freeze water was eliminated completely with the suspension of a very low mass fraction ($0.020 \pm 0.001$ wt%) or surface area concentration ($0.070 \pm 0.003$ $m^2$/ml) of graphene. Compared to nanoparticles of $SiO_2$ and $TiO_2$ with the same mass fraction suspended in water, flakes of graphene led to freeze water at a much smaller subcooling degree, and shorter total freezing time. The addition of surfactants can improve suspension stability and further reduce the degree of subcooling, but it also slightly increases the total freezing time. Graphene flakes are more suitable than spherical oxide nanoparticles for use as nucleating additives in water.



## 1. Introduction

Energy conservation and environment protection are very important topics in the field of energy. Cool thermal energy storage has become one of the primary solutions to the electrical power imbalance between daytime need and nighttime abundance [1]. Ice storage technology is a kind of common cool storage technology. Water has large latent heat and is usually used as working medium to storage the electric energy in the nighttime [2]. However, the problems of large subcooling degree and poor thermal conductivity limit the development of ice storage technology. The large subcooling degree will lower the evaporating temperature of the refrigerator and reduce the refrigeration efficiency. In addition, the low thermal conductivity of pure water limits the performance of energy storage devices [3]. Thus, the elimination of subcooling and enhancement of thermal conductivity are highly important.

Nanofluids are created by dispersing solid nanoparticles in a fluid to enhance their properties, such as heat transfer rate [4]. The use of water-based nanofluids in ice storage technology has been proposed in recent years [5], because they have a higher thermal conductivity than pure water [6]. Preliminary evidence indicated that water-based nanofluids undergo a small degree of subcooling in solidification because these nanoparticles can act as nucleation additives to promote heterogeneous nucleation [7–9]. For example, Mo et al. [7] investigated the crystallization

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**Nomenclature**

| | | | |
|---|---|---|---|
| $c$ | concentration | $T_s$ | subcooling temperature |
| $T_p$ | phase change temperature | $m$ | subcooling degree reduce |
| $\Delta T$ | subcooling degree | $k_e$ | thermal conductivity enhance |
| $K$ | thermal conductivity | $n$ | total freezing time reduce |
| $t$ | total freezing time | $h_r$ | phase change heat reduce |
| $h$ | phase change heat | | |

behaviors of $TiO_2$–water nanofluids and deionized water by DSC. The $TiO_2$–water nanofluids had higher crystallization temperatures compared with deionized water, and it is more suitable than deionized water for the weight fraction of 0.30% and 0.70% at the cooling rate range of 1.5–9.0 °C/min for ice storage system. Li et al. [8] performed experiments of cool storage feature for Cu–$H_2O$ nanofluids. The subcooling degree of Cu–$H_2O$ nanofluids was reduced by 78.3% with nanoparticle mass fraction 1.0%. Wu et al. [9] investigated the thermal properties of $Al_2O_3$–$H_2O$ nanofluids and concluded that the subcooling degree was reduced by 70.9% with suspending 0.2 wt% $Al_2O_3$ nanoparticles in water. We found that most of the nanomaterials in these researches used to act as ice-nucleating substrates were hydrophilic metal or metal oxide nanoparticles, and their nucleation effect was not strong enough to eliminate the subcooling of water completely. As it well known, particle size [10] and surface area [11] of nanomaterials except for the contact angle are also important factors influencing the heterogeneous nucleation of aqueous suspensions. Up to now, however, stable aqueous suspensions of metal or metal oxide nanoparticles were very difficult to achieve due to the large densities of these nanoparticles, as a result, the concentration of these suspensions were generally not high, not exceeding 1 wt% [12]. We therefore considered that the insufficient surface area of metal and metal oxide nanoparticles exposed to water might be the reason for the limited effect of them on the subcooling of water. Based on the above analysis, we assumed that using certain nanomaterials of large specific surface area as nucleating agents might be able to reduce the subcooling degree of water tend to zero by providing sufficient nucleation sites to increase the nucleation rate of water.

Graphene nanoplate is an ideal nanomaterial which has very high specific surface area compared to conventional metal or metal oxide nanoparitcles as far as we know. It is regarded as the "thinnest material in the universe" with tremendous application potential [13,14]. Graphene is predicted to have remarkable properties, such as excellent thermal and electrical conductivity [15,16] and high specific surface area [17]. The intrinsic properties of graphene have generated enormous interest for the possible implementation of graphene in a myriad of devices [18], including liquid crystal devices [19]. In this study, we found that the graphene nanomaterial was ideal for promoting the freezing process of water because of its ultrahigh thermal conductivity and ultrahigh specific surface area. The graphene nanomaterial represents the first hydrophobic nanomaterial to be proposed for use in an ice storage system.

In this paper, hydrophobic graphene, hydrophilic $SiO_2$ and $TiO_2$ nanomaterials were chosen as the nucleating agents, and their nanofluids were prepared by the two-step method with and without surfactants. The freezing characteristics of $TiO_2$–$H_2O$, $SiO_2$–$H_2O$ and graphene–$H_2O$ nanofluids were compared to uncover the main factors determining the nucleation of nanofluids. The effect of concentration on subcooling degree of graphene–$H_2O$ nanofluids was then investigated to establish the conditions required to make the subcooling of nanofluids disappear.

## 2. Material and methods

### 2.1. The preparation of nanofluids

We used graphene (BTR Nano Tech Co., Ltd., China), $SiO_2$ (Aladdin Chemical Reagent Co., Ltd., China), and $TiO_2$ (Shanghai Huzheng Nanotechnology Co., Ltd., China) as the additives in the present study. The transmission electron microscopy (TEM) images of the three nanomaterials are shown in Fig. 1. The graphene nanomaterial had a lamellar structure. Although some of the nanomaterials overlapped, most of the materials were very thin and well dispersed (Fig. 1a). A few of $SiO_2$ and $TiO_2$ nanoparticles had aggregated, but most of them were well dispersed. The average particle

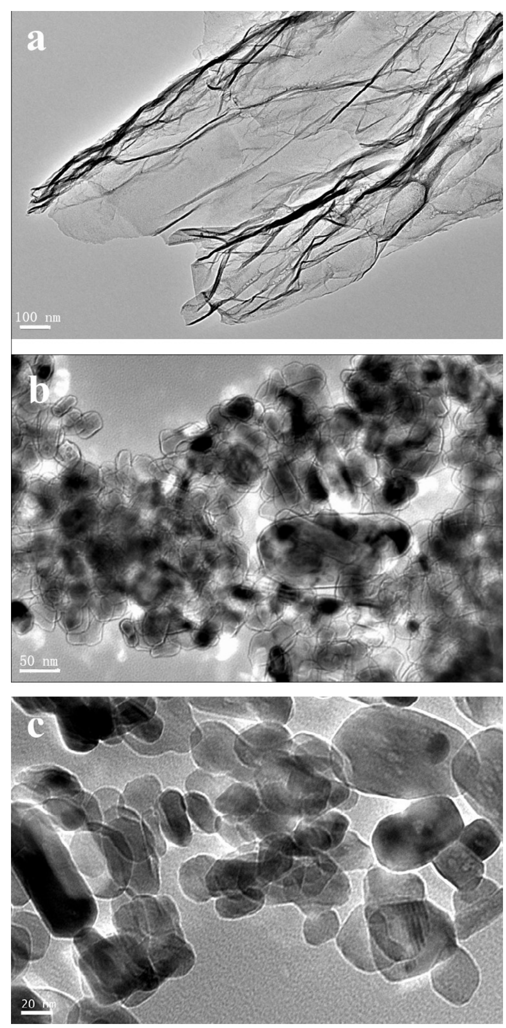


**Fig. 1.** TEM images of (a) graphene sheets, (b) $SiO_2$, and (c) $TiO_2$ nanoparticles.