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Processing of 2D-MAXene nanostructures and design of high thermal conducting, rheo-controlled MAXene nanofluids as a potential nanocoolant

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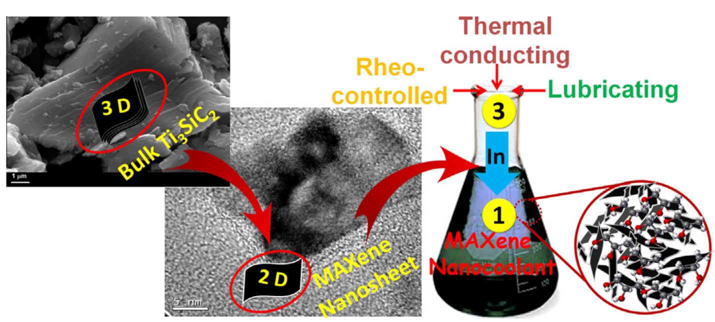
HIGHLIGHTS

- 2D Ti_3SiC_2 MAXene nanosheets based nanofluid was developed for the first time.
- This very stable MAXene nanofluid show rheo-controlled flow behavior.
- About 45% enhancement in thermal conductivity was achieved at 323 K.
- The MAXene nanofluid also exhibit lubricating properties.
- These exotic properties make it superior to conventional heat transfer fluids.

GRAPHICAL ABSTRACT



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ABSTRACT

'Nanocoolants' offering extraordinary heat transport property demand new and exotic nanostructures as fillers that can display enhanced thermal conductivity and thermochemical stability for efficient thermal management operations. Herein we report for the first time, the processing of stable MAXene nanofluids using 2D MAXene nanosheets derived from the bulk nanolaminated Ti_3SiC_2 MAX phase ternary carbides via shear induced micromechanical delamination technique. The beneficial multifunctional physical properties of MAXene colloid such as thermal conductivity, viscosity and lubrication effect are assessed and reported. An enhancement of thermal conductivity by ~45% is achieved at 323 K with a loading of 0.25 Vol% MAXene nanosheets. Interestingly, MAXene nanofluids exhibit decreased viscosity than the basefluid revealing that it can act as 'rheo-controlled' nanofluid. It is a unique rheological behavior, not exist in many well established conventional ceramic nanofluids. In addition, MAXene nanofluids also offer lubricating property with very low coefficient of friction (COF) values (<0.1).

1. Introduction

Heat transfer fluids exhibiting non-reactivity and exceptional thermal dissipation characteristics in addition to good thermo-chemical stability over a range of service temperatures have high demand in thermal management operations [1–3]. Practically, clogging in microchannels and poor fluid stability are the very common technical issues realized with classical thermal fluids prepared with conventional metallic particles [4–6]. This prompted researchers to develop 'nanofluids' using water [4] transformer oil [7], mineral oil [8], ethylene glycol [9,10], propylene glycol [11,12], silicone oil [13] basefluids dispersed with engineered particulates possessing high thermal conductivity. Factors affecting the bulk heat transfer in a thermal management fluid are dispersion stability, surface charge characteristics, fluid viscosity and

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the morphology of nanoparticles. They are controlled by optimum use of particulate solid fraction, i.e., the filler fraction in the basefluid [14]. Apart from the usual settling and choking problems, high filler loading increases viscosity and reduces the pumping efficiency, which is essential for mechanical circulation of the nano-fluid coolants. In fact, the viscosity of thermal fluids prepared with high thermal conducting Al_2O_3 [4], ZrO_2 [6], ZnO [12], Fe_2O_3 [15], SiC [16,17] and CeO_2 [18] etc. is quite high even at very low concentrations. Moreover, nano-particulates such as Al_2O_3, SiC and ZrO_2 dispersoids generate mechanical friction and associated frictional heat finally caused damage to mechanical components [19]. Therefore, a balance between thermal conductivity, stability and viscosity is imperative. It calls for new multifunctional nanostructures where desirable dispersion stability, viscosity and thermal conductivity can be reached.

Successive to many oxides, carbides, and nitrides dispersed ceramic thermal nanofluids, research was then shifted to carbon based nanofluids involving CNT nanostructures [20–22]. The very high thermal conductivity (2000–4000 W/mK) make it attractive for application in nanofluids. Unfortunately, in such nanofluids, the non-reactive CNT surfaces, intrinsic van der Waals force and geometrically high aspect ratios caused severe aggregation and make the system less stable. Surfactants were employed to overcome this drawback [23–25]. However, surfactant molecules cause foaming during heating and weaken the overall thermal properties. Moreover, the thermal resistance between CNTs and basefluid may increase due to surfactant molecules attached to the CNT surfaces [26]. Further, the entanglement and associated aggregation in CNT nanofluids causes an increase in viscosity and clogging in microchannels. To overcome this, Xie et al. introduced acid functionalization of CNTs to prepare surfactant free, stable CNT nanofluids [27]. Metal nanoparticle modification of CNTs is another method reported to improve the stability and performance of nanofluids [22].

2D nanostructures like graphene, fluorinated graphene oxide and boron nitride are recently emerged as potentially high thermal conducting, heat dissipative dispersoids in nanofluids to be used as nanocoolants [28–30]. Ramaprabhu and coworkers reported an enhancement of *ca.* 28% in thermal conductivity of water at 25 °C using metal oxide decorated graphene nanosheets [31]. A hybrid approach in which functionalized multiwalled CNTs are attached to functionalized graphene was also reported to prepare stable composite nanofluids with enhanced thermal properties [32]. Ajayan and coworkers explored BN nanosheets as electrically insulating thermal conductive fillers in transformer oil [33].

In this series, design of new 2D nanostructures is quickly growing. Recently our group reported the synthesis of a novel 2D nanostructure namely MAXene nanosheets from bulk Ti_3SiC_2 MAX phase ceramic nanolaminates for the first time [34]. MAX phase is the family of ternary carbides/nitrides denoted as $M_{n+1}AX_n$ where M is an early transition metal, A represents group IIIA, or IVA element and X is either carbon and/or nitrogen. It primarily consists of alternate MX layers separated by A layer atoms. Ti_3SiC_2 is the most familiar MAX phase studied extensively, including applications in structural composites [35–37]. Ti_3SiC_2 ternary carbides are novel engineering material possessing attractive functional properties. It is thermally stable like ceramics with exceptional machinability and thermal/electrical conductivity; features seen with metals. Bulk Ti_3SiC_2 has thermal conductivity in the range 37–40 W/mK [38]. Ti_3SiC_2 is also known for its self-lubricating properties [39]. Since Ti_3SiC_2 has unusual thermal, electrical and lubricating characteristics high interest is there to make multifunctional MAX phase nanostructures. We could produce 2D MAXene nanosheets via shear induced micromechanical delamination technique [34]. A few layers thick Ti_3SiC_2 MAXene nanosheets were found to be very well stable in polar solvents. Since these newly derived Ti_3SiC_2 MAXene nanosheets contain surface terminated hydroxyl groups, they are a promising candidate for obtaining water based thermal-fluids where high thermal conductivity, low viscosity and high lubricating properties can be expected.

Ethylene glycol and propylene glycol are two commonly used water- based fluid in thermal management. Even though ethylene glycol has better heat transport properties, propylene glycol is more non-toxic and environment-friendly than ethylene glycol [40,41]. The excellent antifreeze properties make propylene glycol based fluids one of the fastest growing product segment in heat transfer fluids. Thus, they are used as antifreeze agents in food and beverage industry [40]. Moreover, a liquid with a freezing point less than −40 °C is preferred for electronics cooling. Propylene glycol meets all these requirements. A summary of the demand for heat transfer fluids in the market is presented in Fig. 1. It can be seen that almost all the industries relevant sectors depend on heat transfer fluids to ensure reliable performance. Fig. 1(B) shows the market analysis of various kinds of heat transfer fluids in this decade. It is reported that the global market for all types of fluids is increasing year by year, which indicates the importance of developing new types of high performing fluids.

In the present study, we have successfully prepared a novel high thermal conducting Ti_3SiC_2 MAXene nanofluid in the propylene glycol medium. To the best of our knowledge, this is the first report demonstrating the application of 2D MAX phase nanosheets as heat carriers for heat transfer fluids. Interestingly, we also found unique rheological and lubricating properties in this newly designed MAXene thermal fluid. It is envisaged that the application of this multifunctional rheo-controlled 'MAXene nanocoolant' can contribute to the development of next generation heat transfer fluids.

2. Experimental

2.1. Materials and methods

Nanolayered Ti_3SiC_2 MAX phase (particle size Dav = 13 μm) was procured from 3-ONE-2 LLC, USA. Micromechanical milling was performed using the Ultra-Fine mortar grinder (Retsch-RM 200, Germany) which works on pressure–friction principle. Propylene glycol (Merck India Ltd) was used as the basefluid. An overview of the experimental procedure adopted in the present work is shown in Fig. 2. In a typical experiment 1 g of bulk Ti_3SiC_2 was taken in 15 mL propylene glycol. It was transferred into the ceramic Retsch mortar and subjected to micromechanical milling for 24 h. Before the last hour milling, the volume of propylene glycol was raised to 100 mL. After 24 h, the milled dispersion was transferred to a container and subjected to ultrasonication for 1 h using the ultrasonic processor (Sonics Vibra Cell, 20 kHz). The resultant dispersion was then centrifuged at 8000 rpm to settle down the un-exfoliated large particles. The delaminated Ti_3SiC_2 nanostructures stay suspended in the basefluid was collected for the preparation of nanofluid. The delaminated MAXene nanosheets required for morphological and structural characterization was collected by the removal of propylene glycol through solvent extraction method. For this, the nanofluid was diluted with an excess amount of chloroform and kept for few hours. The nanosheets settled at the bottom were collected by freeze drying. Conventional drying was avoided because it causes restacking of nanosheets. The separated nanosheets were preserved for further characterization. To prepare the nanofluids with various concentrations of Ti_3SiC_2 MAXenes, the solid content of the as processed dispersion was first determined gravimetrically by solid matter determination set up. For this thermal stability of the propylene glycol basefluid was first determined using thermogravimetric analysis (TGA) and it was found that