Recent advances of nanofluids in micro/nano scale energy transportation

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Abstract: As the continuing integration and size deflation of component dimensions in electronic circuits and increase in the number of transistors in modern microprocessor chips, especially for heat dissipation of micro/nano scale devise, traditionally used single phase fluid cannot meet the requirements for highly efficient heat transfer, which thus frequently results in the damage of electrical devices. Consequently, thermal conductivity enhancement of working fluids is of great significance for advanced thermal energy conservation and conversion. Nanofluids, which possess a superior thermal conductive performance, are studied towards an alternative to the traditionally used working fluids, have attracted ample attention within the past decades. In this paper, firstly, we summarized the recent progress in the preparation of nanofluids, in particular for a method involving a covalent concerning reorganization or generation; subsequently, the utilization of nanofluids in hitherto unsummerized micro/nano scale heat and mass transfer fields, especially for some chemistry relating applications were discussed. All works demonstrated in this review are aiming at clarifying the fact that advanced material technologies are required in preparation of recent

nanofluids on the premise of continuing harsh energy transfer situation; on the other hand, nanofluids were also able to offer insights for novel micro/nano scale energy transportation which has not yet been reviewed before.

Keywords: Energy transfer; Nanofluids; Micro/nano scale; Preparation; Application; Heat transfer

Abbreviations

GO	Graphene oxide
MGE	Modified graphene
$Ag\text{-}SiO_2$	Silver-silica
DW	Distilled water
rGO	Reduced graphene oxide
CNTs	Carbon nanotubes
MWCNTs	Multi-wall carbon nanotubes
SEF	System efficiency factor
Re	Reynolds number
FGNs	Functionalized graphene nanoplatelets
SGR	Sulfonated graphene
IL	Ionic liquid
DES	Deep eutectic solvent
GO/TiO_2	Graphene oxide/titanium dioxide
SiO_2	Silicon dioxide
SDBS	Sodiumdodecylbenzenesulfonate
PVA	Polyvinyl alcohol

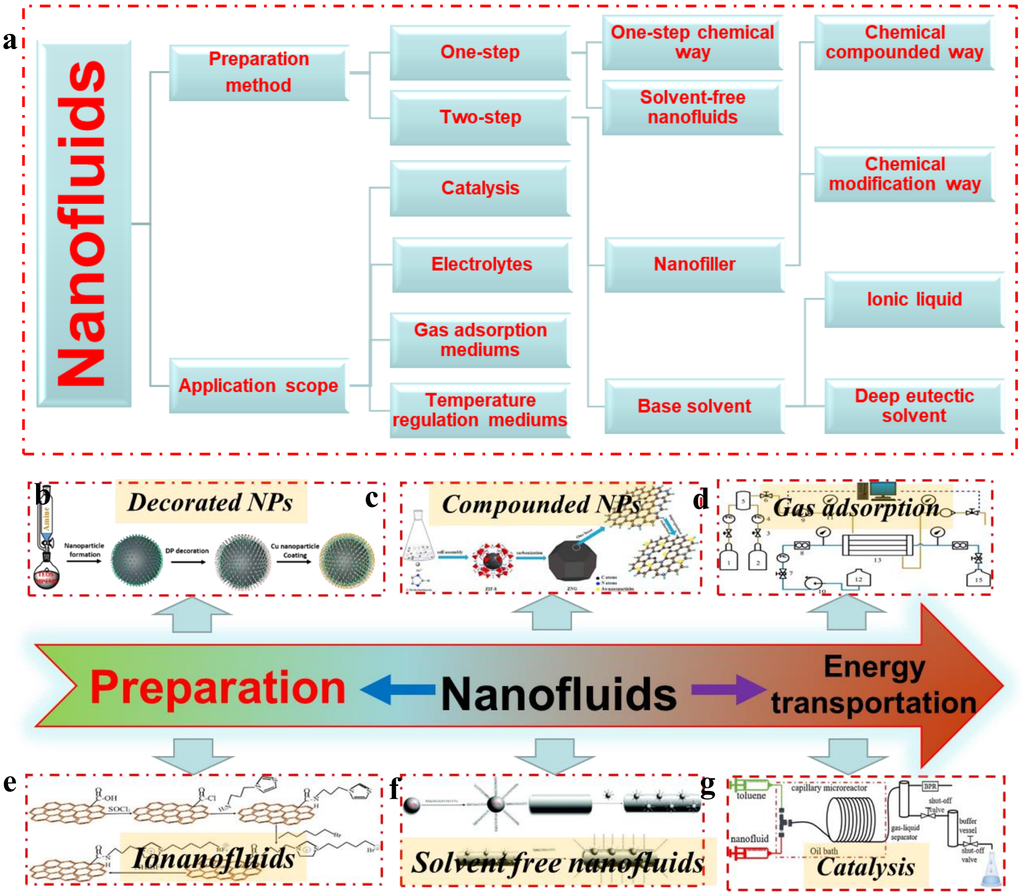
Contents

1. Introduction

As the rapid economy growth and the development of machinery with the continuing integration and size deflation of component dimensions in electronic circuits and increase in the amount of transistors in modern microprocessor chips, especially for heat dissipation of micro/nano scale devise, traditionally used single phase fluid cannot meet the requirements for highly efficient heat transfer [1-5]. Nanofluids, which was firstly coined by Choi in 1995 [6-8], emerged an interesting alternative to a single phase working fluid, have become a hot research topic with the purpose of solving the relative poor thermal conductivity of working fluids.

Nanofluids were generally composed by a base solvent and nanoparticle, integrated through a one-step or two-step pathway. Since the discovery of nanofluids, numerous reports regarding the investigation of their preparation and thermophysical properties [9-14]. However, most of preparation methods rely on a physical blending approach starting from commercially available base solvents and nano materials, where generally no chemical properties change occurred during the preparation process. In the meantime, in some cases, a single material is unable to fulfil all the favorable characteristics requirements for a specific objective [15-17]; it should either exhibit good rheological or thermal properties. However, in a series of practical applications, it is recommended to trade-off between some properties which results in the development of other hybrid nanofluids with the specific characteristics. Additionally, traditionally used base solvent, such as water, alcohol, mineral oil etc. are unable to be used in every situation due to their inherent flaws, for instance, electrical conductive, flammable and narrow liquid temperature range [18-21]. Furthermore, aggregation of nanofillers and aging of nanofluids quite limited the widely utilization of nanofluids for the inhibition of stacking of flowing tube line, therefore, a most applicable fabrication way which could enhance the stability of nanofluids was highly in demand. In these scenarios, chemical modification or fabrication strategies would be an efficient solution to the above-mentioned problems. Hence, one of the objectives of this review is analyzing the chemical transformation or reaction, which allows the formation the nanofluid bearing a wanted property, thus provides a positive reference for further development of nanofluid with a specific utilization purpose.

Micro/nano scale energy transportation emerged an advanced technology has been widely applied in many areas, where prominent examples can be found in energy dissipation of circulation system in human being body [22], massive database system [23], portable or wearable devices [24], or high performance medical instrumentation [25-27]. Nanofluids have been well recognized to be used in heat energy transportation and management. However, owing to this unique characteristic which derived from Brownian motion and nanoscale effect of nanofliller, endows nanofluids with advantageous heat and mass transfer properties, therefore, nanofluids application in some other fields was also being studied.[28, 29] Among them, applying nanofluids to absorb gas, liquid or solid pollutants from the point of view of environment protection, adjusting the chemical reaction proceedings through the regulation of reaction temperature or acting as a catalyst to promote organic chemical reactions etc. in which energy transportation is the dominate factor and also belongs to the energy related application field that should be considered since nanofluids were able to play a key role in those processes, were concerned by few people so far. Out of this consideration, the other purpose of this review is to summarize the recent advances in utilization of nanofluids in a chemical related energy transportation way, to make a supplementary for a vast of reviews with respect to nanofluids using in thermal related fields.



Scheme 1. (a) Main contents of this review. (b) Schematic diagram of SiO_2 nanoparticles modified by dihydropyran and Cu nanoparticles. (reproduced with permission from ref.[30], Copyright (2019) American Chemical Society) (c) Schematic synthesis procedure of Au graphene composite. (reproduced with permission from ref.[31], Copyright (2018) Elsevier) (d) Schematic diagram of the experimental apparatus.(reproduced with permission from ref.[32], Copyright (2015) Elsevier) (e) The process of making the modified graphene (MGE) (reproduced with permission from ref.[33], Copyright (2017) Elsevier) (f) Synthesis of non-ionic nanofluid hybrid materials for nanotube modified by silicon dioxide (SiO_2). (reproduced with permission from ref.[34], Copyright(2009)Elsevier) (g) Schematic overview of the experimental apparatus.(reproduced with permission from ref.[35], Copyright (2018) Elsevier)

2. Preparation of nanofluids through a chemical way

2.1 Preparation of nanofiller through a chemical fabrication way

2.1.1 Synthesis of hybrid nanofillers in a chemical compounded way

Up to date, numerous reports related to the synthesis of nanofluids in a hybrid manner aiming at combining the merits of each component in particular for nanoparticles [18, 36, 37]. The preparation of hybrid materials can be roughly divided into simple physical blending and chemical compounded ways. In this review, we mainly focus on synthesizing nanofluids in a chemical pathway, where covalent bond formation or chemical transformation are involved. Representatively, Xuan et al. developed a Fe_3O_4/TiN Janus nanoparticle filled water based nanofluids by combining the advantages of Fe_3O_4 and TiN, which demonstrated to be high absorptive in near-infrared wavelength and localized surface plasmon resonance in the visible wavelength for TiN and Fe_3O_4 respectively (**Fig. 1a, 1b** and **1c**). As a result of this compositing material, the prepared nanofluid was able to make a full-spectrum absorption of incident solar energy [38]. Integration between Fe_3O_4 and TiN was enabled by a covalent acylation process, in which Fe_3O_4 was decorated by carboxyl group and TiN was modified by amino group, therefore guaranteed a sturdy state of the hybrid nano-materials. Importantly, the as-prepared nanofluids exhibited tuneable thermal physical and optical properties towards external magnetic field owing to Fe_3O_4 component in the hybrid nanomaterial.

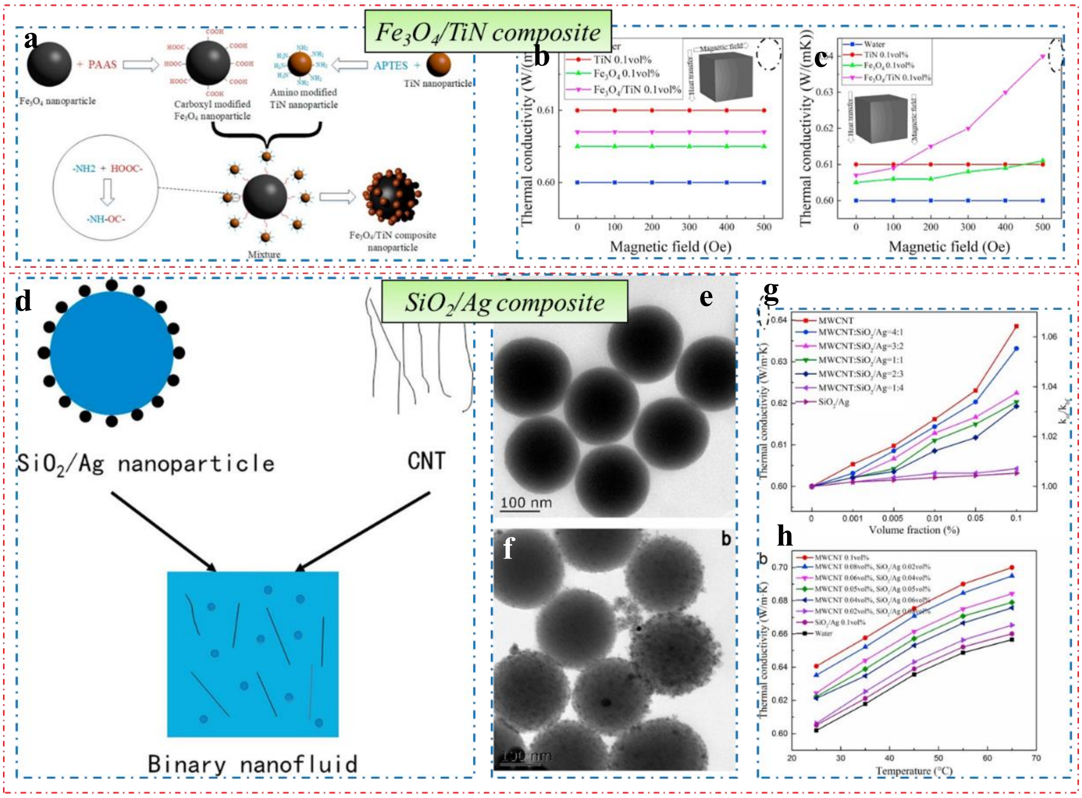


Fig. 2 (a) The preparation technology of composite Fe_3O_4/TiN nanoparticles. (b) The thermal conductivities of water and TiN, Fe_3O_4, Fe_3O_4/TiN nanofluids under different magnetic fields and without magnetic field. (c) The thermal conductivity of water and tin, Fe_3O_4 and Fe_3O_4/tin

nanofluids without and with different magnetic fields. (d) the preparation of SiO_2/Ag binary nanofluid and (e) the TEM images of SiO_2 nanoparticles, (f) the TEM images of SiO_2/Ag nanoparticles, (g) thermal conductivities of nanofluids at room temperature (25 ^{o}C), (h) thermal conductivities of nanofluids prepared by different ratios of multi-wall carbon nanotubes (MWCNTs) and SiO_2/Ag at different temperature. (**Fig. 2a**, **2b** and **2c** were reproduced with permission from ref.[38], Copyright (2018) Elsevier); **(Fig. 2d**, **2e**, **2f**, **2g** and **2h** were reproduced with permission from ref.[39], Copyright (2018) Elsevier).

In order to enhance solar thermal conversion and thermal conductivity of water, Xuan et al. developed a CNT-SiO_2/Ag nanoparticle filled nanofluid using a two-step preparation method (**Fig. 2d**, **2e**, **2f**, **2g** and **2h**) [39]. SiO_2/Ag used in this work was fabricated through an *in-situ* chemical reduction way by using Sn^{2+} as a reduction reagent. Owing to the high absorption in infrared spectra of MWCNTs, and SiO_2/Ag nanoparticles bearing an intense absorption towards visible spectra, the obtained naofluids got much higher absorption rate in a much wider solar spectra range. Meanwhile, thermal conductivity of the nanofluid by filling this kind of nanoparticle was enhanced by 7% with the 0.1% volume fraction of CNT-SiO_2/Ag. Mechanism study revealed that the participation of Ag nanoparticle and linear structure of CNT accounted for the high thermal conductivity of the prepared nanofluids and promising light-to-thermal efficiency.

Similarly, Taylor et al. reported a nanofluid that composed by using a core-shell silver-silica (Ag-SiO_2) and CNTs as nanofiller in a water base solvent [40]. Most of the visible spectrum could be covered by this hybrid materials, thus resulted in promising photovoltaic/thermal conversion efficiency. To better understand the working mechanism of the hybrid nanoparticle composites, modelled and experimental results for a spectrally-tailorable, multi-particle nanofluid filter put between a concentrated light source and a silicon cell was presented. Results showed that a mass fraction of 0.026% of Ag-SiO_2 nanofluids could increase the efficiency by 30% compared with that of the sole base fluid.

Graphene is a mono-layered carbon material and can be used for a promising candidate when acting as a nanofiller to enhance thermal conductivity of nanofluid thanks to its superior thermal conductivity and unique two-dimensional structure. However, it also exhibits comparable electrically conductivity which contradicts with insulating properties when used as a transformer oil additive. To make use of the benefit of high thermal conductivity and inhibiting its electrically conductive properties at the same time, incorporating graphene with an insulated material would open an avenue for vast use of graphene in the field of nanofluid. For instance, Navas et al. developed a series of graphene filled nanofluids, and studied their properties in terms of enhancement high static stability, solar harvesting performance and optical performance by using exfoliation and structure modification on graphene.[41-44] Rashmi et al. synthesized a SiO_2-graphene nanoparticle through a sol-gel technique under a series different pH values ranging from 9 to 12 [45]. Some analyses, including, FESEM, XRD and FTIR, were used to prove the successful embedding of SiO_2 on the surface of graphene. Experimental results revealed that the addition of SiO_2-graphene hybrid nanoparticles could intensively reduce the electrical conductivity enhancement of base fluid from 557% to 97%. On the other hand, because the SiO_2 synthesis technology has been very mature, which can be named as a chemical liquid deposition method, thus coating SiO_2 in the surface of graphene was widely adapted by researchers. For instance, Chen et al. reported a SiO_2-coated grapheme filled nanofluid with the aim at improving the compatibility and stability of graphene in water since SiO_2 could provide this carbon material with superior hydrophilicity, chemical inertness, biocompatibility [46]. Additionally, in this work, nanofluids filled by this hybrid material afforded a higher thermal conductivity enhancement compared with that of dispersant aided graphene nanofluids.

Coating graphene oxide (GO) with anatase TiO_2 through a facile solvo-thermal method for the preparation nanofluids which possessing lubrication ability was demonstrated by Sun et al [47]. The investigation revealed that the hybrid GO nanosheet had a largest thickness of 28.07 nm, which was determined to be nanoscale. And the rolled strip lubrication nanofluid had negligible defect and minimum roughness. Moreover, the author claimed that the superior lubrication properties was due to the promising dispersion stability and the generation of some absorption films owing to the existence of TiO_2 component in the hybrid material.

Mehrali et al. prepared a Fe_3O_4 grafted rGO composite by employing two-dimensional GO nanosheets, iron salts as starting materials, tannic acid as both reducing and stabilizing agents (**Fig. 3a, 3b** and **3c**) [48, 49]. Graphene sheets in this work was mainly responsible for thermal conductivity of the nanofluid, while the ferric component contributed magnetic property to this composite which offered a tunable thermal physical property under the external magnetic field. Study upon the fluidic property showed that a Newtonian fluid characteristic, magnetic performance of the nanofluid exhibited that superparamagnetic properties of the nanofluid was verified from its saturated magnetic value of 45.9 emu/g. Interestingly, experimental results showed the thermal conductivity enhancement of the as-prepared nanofluid was negligible over pure water, while, the heat transfer coefficient of the nanofluid could be increased by 82% under a permanent magnetic force, which clearly illustrated the heavily dependence on magnetic field of this nanofluid.

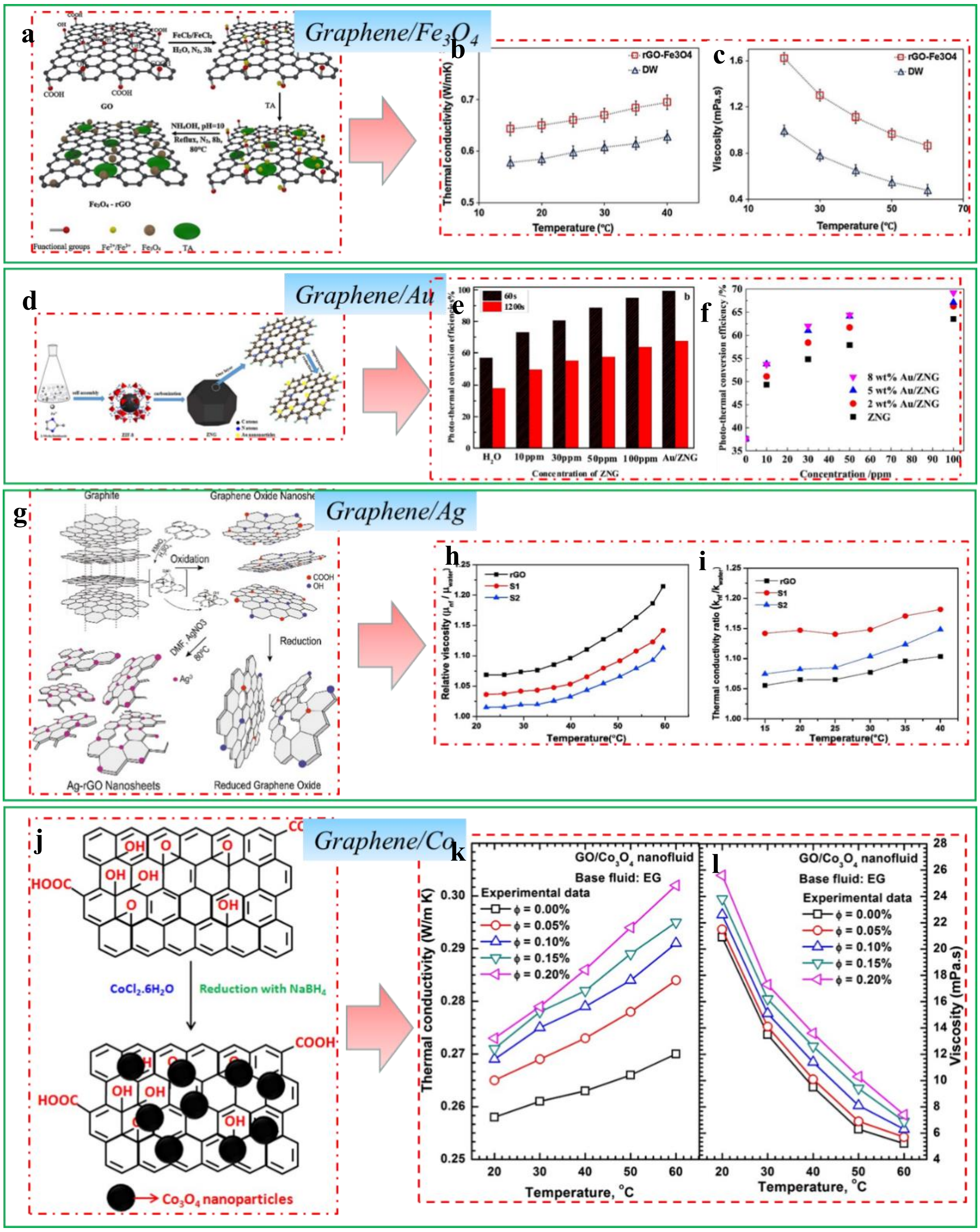


Fig. 3 (a)Schematic of graphene ferromagnetic nanofluid synthesis.(b) Thermal conductivity plot and (c) the viscosity profile of distilled water (DW) and reduced graphene oxide-Fe_3O_4 (rGO-Fe_3O_4) nanofluid. (d) Schematic diagram of the experimental procedure (e) Instantaneous photothermal conversion efficiency of nanofluids with different concentrations of the obtained ZIF-8 (ZIF denotes zeolitic imidazolate framework) based nitrogen-doped graphitic carbon (ZNG).(f) Solar energy efficiency of ZNG and Au/ZNG nanofluids under different Au loads. (g) Schematic diagram of reduced graphene oxide (rGO) and AG-RGO nanocrystals using DMF as catalyst. (h) Relative viscosity and (i) thermal conductivity ratio as a function of temperature for nanofluids with a concentration of 100 ppm. (j) Synthesis procedure of GO/Co_3O_4 hybrid nanoparticles. (k) Experimental thermal conductivity and (l) viscosity of EG-based GO/Co_3O_4 hybrid nanofluids. (**Fig. 3a**, **3b**,**3c** were reproduced with permission from ref. [48], Copyright (2017) Elsevier) (**Fig. 3d 3e**,

3f were Reproduced with permission from ref.[31], Copyright (2018) Elsevier) (**Fig. 3g**,**3h, 3i** were reproduced with permission from ref.[50], Copyright (2018) Elsevier) (**Fig. 3j**,**3k, 3l** were reproduced with permission from ref.[51], Copyright (2017) Elsevier)

Fe_3O_4 incorporated graphene composite that prepared through a chemical reduction deposition method was also studied by Rashidi et al [52]. By using this graphene composite as nano-additive of kerosene, thermal conductivity could be significantly improved by 31% at 50 °C. Moreover, the heat transfer enhancement could reach to 66% at Reynolds number (Re) of 4553 and 0.3 *wt*.% of nanoparticle.

Yu et al. firstly synthesized a nitrogen doped graphene and impregnated Au on the skeleton of graphene (**Fig. 3d**, **3e** and **3f**) [31]. Photo-to-thermal conversion testing indicated that the Au decorated graphene exhibited broad band absorption from the visible to near infrared region, which ensured an obvious improvement in photo-to-thermal performance thanks to the cooperative effect of the plasmon resonance Au nanoparticle. Mehrali et al. demonstrated a graphene/silver filled water based nanofluid for Solar energy harvesting (**Fig. 3g**, **3h** and **3i**) [50]. In this work, the hybrid nanoparticle was fabricated through an *in-situ* chemical reduction strategy, and the results proved that Ag nanoparticles were uniformly decorated on the skeleton of reduced graphene. Their superior solar absorptance and thermal conductivity was attributed to the plasmonic effect of the nanoparticles and high thermal conductivity of graphene nanosheets, respectively. Further investigation revealed that the solar collector can achieve to 77% at a low concentration of 40 ppm. Additionally, the uniform Co_3O_4 dispersed GO nanosheet was prepared by Sundar et al. for the nanofluids with high thermal conductivity and good stability (**Fig. 3j**, **3k** and **3l**) [51]. GO/Co_3O_4 hybrid nanoparticle in this work was synthesized through an *in-situ* growth and chemical co-precipitation method using $CoCl_2 \cdot 2H_2O$ as a precursor and $NaBH_4$ as a reductant. Experimental results showed that the thermal conductivity of water and EG can be enhanced by 19.14% and 11.85%

respectively in the presence of this type GO/Co_3O_4 hybrid nanoparticle at a testing temperature of 60 °C.

Besides coating with some inorganic metal oxide, graphene was also studied upon compounding by a metal nanoparticle for the further thermal conductivity improvement. For example, Bahiraei et al. developed an *in-situ* chemical reduction methodology for the synthesis of graphene nanoplatelet–platinum composite [53]. The investigation of the as-prepared nanofluids in a triple-tube heat exchanger equipped with inserted ribs was also conducted. Nanofluids containing graphene-silver nanoparticles were also reported by the same group, the author studied thermal performance and the second law properties of the two new microchannel heat sinks by operating with this kind of Ag-graphene filler nanofluid [54]. Besides, utilization in thermal management on CPU cooling of this nanofluid was also studied by the same group [55]. Moreover, graphene-silver nanoparticles, which prepared through a chemical reduction method, filled nanofluid was also reported by Yarmand et al., as indicated in the experiment results, a significant thermal conductivity improvement, 22.22%, was obtained at a mass fraction of 0.1% particle under a temperature of 40 °C [56]. Ag decorated graphene nanoparticle was also studied and applied to prepare nanofluid by Yarmand [57] and Su [58].

A nitrogen doped activated carbon/graphene composite was fabricated by Gharehkhani et al [59]. It should be mentioned that the nitrogen was introduced through pyrolysis of a waste material fruit bunch pulp. Elementary mapping analysis proved that nitrogen was evenly distributed on this material. Thermal physical properties toward this carbon/graphene composite filled nanofluid revealed that thermal conductivity could be enhanced by 10.16% compared with that of base solvent. Moreover, electrical conductivity of this carbon based nanofluid could be remarkably improved by

11433%.

Besides chemically metal or metal oxide decoration strategies, reports regarding the synthesis of hybrid graphene in a bio-inspired method was also found in some literatures for enhancement of bio-compatibility and stability. For example, Sadri et al. developed a facile, bio-based novel approach for fabrication of a covalently functionalized graphene nanoplatelet with the aim of thermal conductivity enhancement (**Fig. 4a** and **4b**) [60]. Eugenol, β-caryophyllene and eugenyl acetate were extracted from dried clove buds, which is an aromatic flower bud, widely found in tropical counties, was suspended and covalently grafted on the skeleton of graphene. Rheological performance of this kind of nanofluid showed that there was a significant enhancement in the convective heat transfer coefficient and Nusselt number, while a negligible improvement in friction factor and pumping power was observed for this nanofluid.

Carbon nanotubes (CNTs) bearing outstanding chemical, electrical, thermophysical and catalysis properties thus have been paid much efforts [61-63]. However, it is recognized that lacking of solubility and the inherent physical and chemical inertness hampers their application in heat transfer field, especially for its application in nanofluids. Hence, functionalization or decoration on the side walls are quite necessary for CNTs when used in a solvent system. Out of this consideration, Hosseini et al. developed a covalently functionalized carbon nanotube in an environmental benign way (**Fig. 4c** and **4d**) [64, 65]. The key of the preparation method in this work was covalently bonding formation between MWCNT with clove buds, and the main component was determined to be eugenol that could be covalently associated with CNTs using a free radical grafting reaction. Notably, thermal conductivity of this MWCNT dispersed nanofluid could be enhanced by 20.15% for a nanoparticle mass fraction of 0.175% at 50 °C. Meanwhile, this kind of nanofluid exhibited excellent stability that it did not display sedimentation over the course of 63 days owing to the functionalization of eugenol who offered a good affinity to MWCNT due to the existence of hydroxyl group on it. Further, numerical studied for this kind of nanofluid was performed by the same group for its turbulent heat transfer property [66]. Teng et al. developed a novel preparation process for highly efficient production of hybrid carbon, which mainly consisted of amorphous carbon, GO, and graphite-2H, by using an acetylene flame synthesis system (**Fig. 4e** and **4f**)[67, 68]. After obtaining the hybrid carbon material, water based nanofluids by filling this carbon material was fabricated and utilized into air-cooled heat exchange system. Results showed that system efficiency factor (SEF) of the hybrid carbon nanofluids could achieve to 11.7% compared with that of pure water.

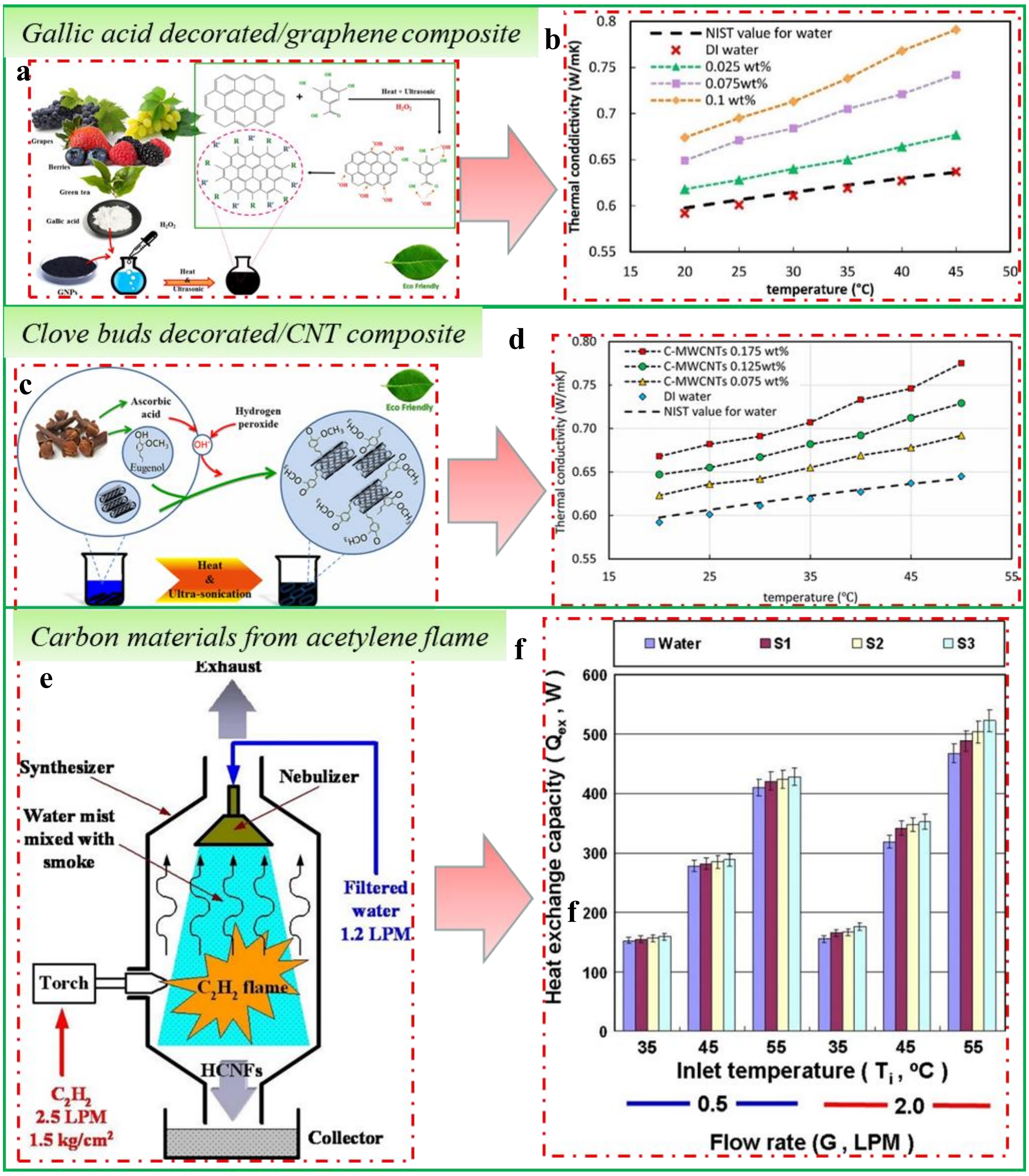


Fig. 4 (a) The mechanism of GAGNPs functionalization method.(b)Thermal conductivity of GNPs suspension and deionized water treated with GA (c) Schematic diagram of carbon nanotube program.(d) Thermal conductivity of the clove-treated multi-wall carbon nanotubes (C-MWCNT-DI) with DW nanofluids and DI water (e) schematic of the acetylene flame synthesis system for hybrid carbon nanofluids. (f) Test sample Re at different inlet temperature and flow rate. (**Fig. 4a** and **4b** were reproduced with permission from ref.[60, 69], Copyright (2017) Elsevier.)(**Fig. 4c** and **4d** were reproduced with permission from ref.[64], Copyright (2017) Elsevier) (**Fig. 4e** and **4f** were reproduced with permission from ref.[67], Copyright (2017) Elsevier)

He et al. reported to integrate CNT with Fe_3O_4 through a chemical reducing deposition method starting from $FeCl_2$ and $FeCl_3$ with the aid of reductant vitamin C [70]. The decorated CNT can be easily separated from water at a rate faster than that of the sole Fe_3O_4 under a condition of external magnetic field. The thermal receiver efficiency could reach to 88.7% with a 0.5 g/L Fe_3O_4/CNT nanofluid. More importantly, the recovery rate and efficiency can be facilely adjusted by tuning the magnetic field strength. Besides the aforementioned approaches, Navas et al. studied an interesting interfaced-inspired formulation and molecular-level effect on a CNTs based nanofluid, this concept mainly arised from the rationalisation of the minimum tension at the interface between a filling nanoparticle and a based fluid.[71] Moreover, examples demonstrated the chemical hybrid CNTs nanomaterials for using in nanofluids were summarized in Table 1.

Table 1. A summary of CNTs hybrid nano materials that used in nanofluids.

Hybrid material	Hybrid method	Base solvent	Ref.
Fe, Al metal oxide	Thermal CVD reaction	poly-alpha-olefin	[72]
Silica nanosphere	Wet chemical method	Water	[73]
Silica	Wet chemical method	Glycerol	[74]
Graphene	Surface modified with COOH or OH groups	EG	[75]
Cu decorated graphene-MWCNT	Chemical reduction method	EG	[76]
TiO_2	Chemical hydrolysis technique	Water	[77]
TiO_2	Chemical hydrolysis technique	Water	[78]
Fe_3O_4	Chemical in situ gro*wt*h method	Water	[79]

Fe_3O_4	Chemical in situ gro*wt*h method	Water	[80]
Al_2O_3	Solvo-thermal process	Water	[81]
Ag-hydrogen exfoliated graphene	Chemical reduction method	EG	[82]
Graphene	Chemical vapor deposition	EG and water	[83]

2.1.2 Preparation of nanofillers through a chemical modification way

Chemically compounded protocol offered a new avenue for the wide application of nanoparticle with some designed wanted properties. Another approach to access the goal is rendering a covalently modification by grafting some specific functional groups. Typical example can be found when graphene was used as a substrate. As above mentioned, graphene is a honeycomb structured monolayer of sp^2-bonded carbon based material, which has gained much attention due to the specific two-dimensional structure, exceptional chemical and physical properties [84, 85]. It should be noted that thermal conductivity of a single layer graphene is reported to be able to achieve to 5000 W·m^{-1}·K^{-1} [86]. Inspired by the superior thermal conductivity of graphene, study upon its using in nanofluid preparation has been intensively studied [87-89]. While, poor stability in a polar solvent system of graphene derived from the intrinsic hydrophobic property much hampered its way for widely using. In order to solve this problem, Yu et al. developed a dispersant MGE nanosheets through an *in-situ* coating strategy before the occurrence of the reducing process in a modified Hummer's method [88, 90], by which the stability of the nanofluid in a polar solvent, EG, was much improved. Thermophysical properties regarding this nanofluid revealed that thermal conductivity can be heavily enhanced by 86% with 5.0 vol. % of MGE.

Zhai et al. reported a phenyl-sulfonic functionalized graphene, which was fabricated through a sequential chemical oxidation and sulfurization process, and applied it in nanofluid with the purpose of enhancing the electrical conductivity and thermal conductivity of the nanofluid. Experimental results revealed that MGE material displayed good affinity with water, thus guaranteed a good stability of as-prepared water based nanofluids [91]. Notably, this work provided a new understanding regarding the electric-field-tunable property of the synthesized nanofluid which might have many potential applications.

lsadri et al. fabricated a highly stable chemically MGE nanofluids by using gallic acid through a one-pot free radical grafting strategy [69, 92, 93]. Because of the acid structure (phenol) and green properties, gallic acid could be a promising candidate for the further functionalization of graphene. H_2O_2 used in the procedure was firstly decomposed into a hydroxyl radical to initiate the radical coupling between graphene and gallic acid. In addition, H_2O_2 is an environmental friendly radical initiator that water is the sole product of the reaction. Rheological study revealed that this gallic acid MGE provided obvious increase in Nusselt number and convective heat transfer performance, while slight rising on friction factor and pumping power was observed, clearly proved the promising performance of the MGE material. Diamond is of great interest when employed as a nanofluid additive owing to its high thermal conductivity, hardness, and low electrical conductivity [94, 95]. However, its inherent hydrophobic property quite limited the wide use in preparation of nanofluids. Generally, gas annealing techniques or addition of a dispersant could make a better performance in terms of stability and fluid property [96]. Covalently modification of nanodiamond provided an efficient way to achieve permanent stable nano diamond filled nanofluid by changing the surface characteristic. Representatively, Lukehart et al. developed a glycidol monomer surface modified nano diamond using an esterification reaction between the two components [97]. The prepared covalently modified diamond nanoparticle was proven to be highly stable in an EG based solvent and exhibited 12% thermal conductivity enhancement at a diamond nanoparticle concentration of 0.9 vol %. Besides the aforementioned chemical compounded way, chemical modification was also feasible towards the fabrication of CNTs with the purpose for either enhanced static stability or thermal conductivity, some typical examples were listed in table 2.

Table 2. Typical examples of chemical modification of CNTs for either enhanced static stability or thermal conductivity of nanofluids.

Nanoparticles	Chemical method	Base fluid	Enhancement	Remark	Reference
Oxygen functionalized CNTs	Functional group modification	Ethanol	Not available	Keep stable for more than one year	[98]
Carboxyl-functionalized MWCNTs	Chemical vapour deposition technique	Water	0.08 vol % results in a 7.26% thermal conductivity enhancement	The thermal boundary resistance and the thermal boundary conductance of MWCNT–COOH/water were found to be 90×10^{-8} m^2	[99]

				KW^{-1} and 1.1 MW m^{-2} K^{-1}	
Carboxylic acids-treated MWCNTs	Direct coupling	Water	0.2 vol % results in a 0.27% thermal conductivity enhancement	Not available	[100]
CuO-MWCTNs	Covalent functionalization	Water	0.06 *wt.* % results in 7.2% enhancement		[101]
Amine-functionalized MWCNTs	Chemical vapor deposition	Water	Not available	The CO_2 absorption capacity of this nanofluid is 36% higher than that of water	[102]
MWCNT-Ag	Covalent functionalization	Water	1 *wt.* % results in a 35%	Thermal efficiency: MWCNT-Ag (1*wt.* %)>MWCNT- Ag	[103]

thermal conductivity enhancement	(0.5 *wt*%)>MWCNT (1*wt.* %)>MWCNT (0.5 *wt*%)>water

Boron nitride nanosheets, which are termed to be “white graphene”, are composed of several monolayer of hexagonal boron nitride. They exhibit a similar structure to that of graphene and have received much attention in recent years [104-106]. Notably, compared to graphene, they have a relatively lower density and electrical insulation, which led them to be a more desirable candidate in the field of nanofluid. However, exfoliation boron nitrides into few-layer boron nitride nanosheets has become one of the main obstacles for imposing it into nanofluids since it has an obvious effect on the thermal conductivity enhancement rate and stability of the final stage nanofluid. Based on this principle, Ajayan et al. used a liquid exfoliated method in isopropanol, and the nanofluid was obtained by redispersion in mineral oil in order to make use of the nanofluids as a kind of transformer oil [107]. Yu et al. reported a molten hydroxide assisted boron nitride exfoliation method to produce boron nitride nanosheet nanofluids [108]. Thanks to the hydroxide aided exfoliated step, the defects on the boron nitride nanosheets was captured by hydroxyl group, by which the affinity between boron nitride nanosheets and water was much improved and thermal conductivity was also enhanced consequently. Remarkably, thermal conductivity of this nanofluid could achieve to 2.39 $W/m^{-1}K^{-1}$ at 24 vol % loading, indicating that the hydroxide modified nanofluids have a predominant thermally conductive performance.

Moreover, Ghosh et al. synthesized dispersed oleic acid wrapped ceria nanoparticles using a simple chemical thermal decomposition of a cerium oleate complex in a high boiling point organic solvent [109]. Oleic acid modification endowed the nanoparticle with high stability. Thermophysical study revealed that 14.6% thermal conductivity was produced at 50 °C with 0.7 *vol.*% solid loading. Chakraborty et al. fabricated a Cu-Al layered double hydroxide nanofluid using a cascade hydrolysis and sonication process [110]. Investigation on its thermophysical properties was studied that a 16.07% of thermal conductivity enhancement was obtained in 0.8 *vol.* % of filling rate. Notably, stability of this nanofluid was excellent that it possessed an approximate +50 mV zeta potential, and no sedimentation can be found after keeping for 4 days. Moreover, recently, several reports are engaged into the preparation of hybrid nanoparticle in either chemically compounded or decorated way. Due to the limitation of text space, some of them were summarized in table 3.

Table 3. A summary of hybrid nano-materials filled nanofluids.

Nanoparticles	Chemical method	Base fluid	Ref.
Functionalized graphene nanoplatelets (FGNs)	Green steam exfoliated	Water	[111]
Polystyrene encapsulated phase change material	Mini-emulsion polymerization	Water	[112]
$Ag+NaSiO_2$ Ag+TEOS	Modified Stöber method	Water	[113]
Sulfonated graphene (SGR)	Chemical vapor deposition method	Water	[114]
MoS_2 nanosheets and MoS_2 nanowires	Liquid phase exfoliation	Eutectic mixture of diphenyl oxide and	[115]

		biphenyl	
β-CD-TiO_2-Ag nanoparticles	Coupling agent modification	Commercially antifreeze	[116]
SnO_2/rGO	Facile low-temperature solvothermal method	Water	[117]
Synthesized SiO_2/ZnO hybrid nanoparticles	Modified sol-gel method	Brine	[118]
Fe_3O_4/Graphene	Hummer's method	Water	[119]
Polyhedral oligomeric silsesquioxane (POSS)-decorated GO (POSS-GO) nanosheets	Solvent evaporation transfer method	Silicone oil	[120]
CuO-chitosan nanocomposites	Covalent functionalization	Water	[101]

2.2 Base solvent fabrication through a chemical approach

2.2.1 Ionic liquid (IL) based nanofluids

Base solvents of nanofluids have a vital position in nanofluids as they determine the basic properties of the resultant nanafluids, such as, thermal conductivity, electrical conductivity, viscosity, boiling point and melting point and so on [121]. Traditionally used base solvents, which could be generally catalogued into water, alcohols and oils, usually suffer from flammability, volatile or relatively narrow liquid range [122-124]. Those drawbacks heavily limit the application scope of nanofluids in specific using requirements. To alleviate the contradiction, ionic liquids (ILs), generally prepared through a synthetic chemical way, act as newly type of working fluids have been attracted ample attention in heat transfer and thermal storage application owing to their unique thermo-physical and chemical properties. In particular, non-flammability, non-volatility, chemical inertness and wide liquid range features of ILs, make them quite applicable as green working fluids for many chemical processes [125-127]. Recently, Moraveji et al. developed a FGNs filled ionic based nanofluid and studied upon its thermo-physical properties, such as viscosity, electrical conductivity and surface tension [128]. Experimental results illustrated that the viscosities of nanofluids decreased as the temperature increasing. Interestingly, the decreasing of viscosity can be observed when enhancing the concentration of nanoparticle. In this work, to ensure a good dispersity in BMIM-PF_6 (1-butyl-3-methylimidazolium hexafluorophosphate), the graphene nanoplatelets was modified by polycarboxylate. In order to understand the exact heat transfer mechanism of IL based nanofluids, Oster et al. performed an experimental work using a series of ILs and nanofillers [129]. From the results obtained in this work and a comparison between reported literatures, the authors found that the nano-layering on the nanoparticle surface was responsible for the specific heat capacity enhancement.

Owing to the extreme low vapor pressure and high thermal stability of ILs, it has been widely adopted in solar harvesting equipment [130, 131]. For example, Zhang et al. reported a graphene filled [HMIM]BF_4 ILs nanofluid [132]. By setting a measurement setup, the solar harvesting efficiency was measured and calculated. It was found that the receiver efficiency could be kept at 0.7 in a 5 cm receiver depth under a 20×1000 W m^{-2} sunlight irradiation strength under the condition of 0.0005 *wt.*% of graphene. Improving the affinity between base solvent and nanoparticle is an efficient way to improve the stability of IL based nanofluids. As a proof of concept, Zhang et al. prepared an ionic-liquid MGE, compared to the graphene without modification, this kind of graphene exhibited superior stability in MGE/[HMIM]BF_4 base solvent [133]. Consequently, IL MGE filled nanofluid displayed enhanced solar receiver efficiency as compared to that of non-modified one, which clearly illustrated the importance of the dispersive efficiency of graphene in IL environment. Zou et al. also prepared an IL based nanofluid for highly efficient sunlight absorption. The addition of SiC in IL could result in a clear thermal conductivity rising and specific heat capacity that 0.06 *wt.* % of SiC increase the thermal conductivity by 10.2% [134]. Viscosity of the nanofluids dropped as the increasing of weight fraction of SiC. Additionally, the optical experimental results showed that SiC played a positive effect on solar absorption where the extinction coefficient of 0.03 *wt.*% SiC IL nanofluids could increase by 5.8 cm^{-1}. Additionally, Khan et al. studied Al_2O_3 nanoparticle enhanced IL based nanofluids by dispersing Al_2O_3 nanoparticles in 1-butyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide, ([C_4mim][NTf_2]) ILs for concentrated solar power applications. The experimental study investigated the effective thermo-physical properties and forced convection heat transfer under laminar and turbulent flow regime.

The results show that thermal conductivity and heat capacity enhanced up to 11% and 49% respectively for the addition of 0.9 *vol.* % Al_2O_3 to the base IL. Zhao et al. developed an IL based nanofluid from MWNTs and 1-ethyl-3- methylimidazolium diethylphosphate [EMIM][DEP], or its aqueous solution[EMIM][DEP](1)+H_2O(2) without addition of any dispersant [135]. Thermal conductivity of the obtained nanofluid was studied that thermal conductivity enhancements ranging from 1.3% to 9.7% in this work. Temperature also affected the thermal conductivity of the nanofluids that a linear correlation was found between testing temperature and the thermal conductivity value. Whereas, the addition of nanofiller showed a negative effect on the viscosity of the nanofluid that a remarkable increase over those of base fluids were found.

Besides application in thermal storage or management field, it was also reported to be capable of being used as an efficient electrochemical sensor for IL based nanofluids. Xu et al. demonstrated an IL based nanofluid, which was prepared through extraction reduction method by using 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIm][PF_6]) as a base solvent, poly(vinylpyrrolidone) as both a extracting reagent and a dispersant, and gold nanoparticles as nanofillers [136]. Experimental study indicated that this kind of nanofluid senor exhibited promising selectivity and reproducibility and sensibility towards human urine samples. Additionally, some other examples for IL based nanofluids were presented in table 4 because of the limitation of the text space.

Table 4. Summary of IL based nanofluids.

Base Fluids	Nanoparticles	Applications	Ref.
1-Butyl-4-methylpyridinium chloride	Fe_2O_3	Solar energy harvesting	[137]
C_2MIMBF_4,	Fe_3O_4	Magnetic	[138]

C_4MIMBF_4, C_6MIMBF_4		lubricant	
$[BMIM][BF_4]$	Nanodiamond	Heat transfer	[139]
$[P_{66614}][N(CN)_2]$, $[P_{66614}][Br]$, $[C_2mim][SCN]$, $[C_4mim][SCN]$, $[C_2mim][C(CN)_3]$, $[C_4mim][C(CN)_3]$	MWCNTs	Heat transfer	[140]
$[Deim][NTf_2]$	$[\beta((MeO)_3Sip)im][NTf_2]$-tethered Al_2O_3	Heat transfer	[141]
$[C_4mim][NTf_2]$	Al_2O_3	Solar energy harvesting	[142]
$[HMIM][NTf_2]$	Ni/C	Direct absorption solar collectors	[130]
$[Bmim]PF_6$	MWCNTs	Heat transfer	[143]
$[C_4mim]BF_4$, $[C_4mim]PF_6$	MWCNTs	Heat transfer	[144]
$[P_{6,6,6,14}]Cl$	AgI nanoparticle	Heat transfer	[145]
$[C_4mim][(CF_3SO_2)_2N]$, $[C_2mim][EtSO_4]$	MWCNTs	Heat transfer	[146]
$[P_{8\,8\,8\,12}][OAc]$,	CuO	Catalysis	[147]

[C$_4$mim][OAc]	Cu$_2$O		
[C$_4$mim][NTf$_2$], [C$_6$mim][NTf$_2$], [C$_8$mim][NTf$_2$], [C$_4$mim][CF$_3$SO$_3$], [C$_2$mim][EtSO$_4$], [C$_4$mim][BF$_4$], [C$_4$mim][PF$_6$]	MWCNTs	Heat transfer	[148]
[Bmim][PF$_6$]	Au nanoparticle	Heat transfer	[149]
[Bmim][PF$_6$]	Functionalized-MWCNTs	Heat transfer	[150]

2.2.2 Deep eutectic solvent (DES) based nanofluids

Despite various attractive features of IL based nanofluids, the application of IL has been less favorable due to the high cost, difficult to prepare and safety uncertainties. DES, which prepared from two or three components through a hydrogen bonding association, emerged an attractive IL alternative has been intensively studied in catalysis, electrochemistry and material chemistry [151]. Owing to its simple preparation procedure, environmental benign properties and easily accessible starting materials, it would be a more promising candidate for a base solvent of nanofluid. While, the study regarding its thermo-physical properties is rare to be seen in literatures, the reason might rely on the fact that DES is a solvent system mainly applied by chemist, researchers in thermal management are not familiar with this matter. However, as the blooming of DES, the investigation in nanofluids is gradually initiated and seen. For example, Walvekar et al. studied the static stability and thermo-physics of DES based carbon nanotube nanofluid [152]. In this work, the author made a comprehensive study on the effect of DES that different types of DESs derived from phosphonium halide and ammonium halide salts were synthesized and subjected to prepare nanofluids. It was found that phosphonium based DESs exhibited the optimized stability performance. The highest thermal conductivity enhancement, 30%, was observed in the case of ammonium DESs based nanofluid, whereas negative thermal enhancement was observed in that of phosphonium DESs based nanofluids. Besides CNTs filled nanofluids, graphene was used to prepare nanofluids with the same constituents of DESs researched by the same group [153]. It was found that the highest thermal conductivity could reach to 177%, and it provided a novel type of engineered fluid for thermal management application.

Liu et al. reported a glycerol/chlorine chloride DES based nanofluid, thermal conductivity enhancement of the as-prepared nanofluids ranged from 3.0 to11.4% by filling nanoscale of GO, TiO_2 and Al_2O_3 [30, 154]. Particularly, nanofluids obtained in this work can be kept as a liquid state at a temperature range from -35 to 275 ^{o}C. The temperature dependent viscosities were studied and it was found that the concentration of nanofiller showed a slight effect on the viscosity of those of nanofluids. Specific heat capacities of the DESs based nanofluids were also studied. Notably, the author provided a chemical approach, FTIR and ^{1}HNMR to study the heat transfer mechanism behind, and indicated that hydrogen bond between base solvent and nanoparticle acted an important role in heat transfer of the nanofluid as it determined the motion activity of the glycerol molecule.

2.3 Fabrication of nanofluid through one-pot chemical method

2.3.1 Synthesis of nanofluid through a one-step chemical pathway

The main nanofluids fabrication method can be divided into two-step and one-step methods. One-step method possessing a more stable property compared to two-step method since the formation of nanoparticle was proceeded simultaneously with the dispersing them into a base solvent, which could thus ensure a superior dispersing efficiency. So, the predominant feature of the one-step preparation of nanofluids mainly lies on the excellent stability. While, as a compensation, the preparation method is usually more complicated than that of two-step fabricated way, which usually relies on a chemically converting process. For example, Gedanken et al. prepared a ZnO nanoparticle filled nanofluid *via* a one-step chemical decomposition method [155]. The key of this work was the high stable colloidal state ZnO in an aqueous medium with the aid of a biocompatible polymer as a stabilizing agent. ZnO nanoparticle was then produced under a treatment with ammonium hydroxide by irradiating with a high intensity ultrasonic Ti-horn. Owing to the superior stability as well as the biocompatibility of polyvinyl alcohol (PVA), this ZnO nanofluid was perhaps to be able to employ as a potential antibacterial agent for practical application.

Qu et al. applied a CuO precursor to premix with water to prepare a super stable $Cu(OH)_2$ colloidal [156]. The material could expose in a microwave oven for several minutes to ensure the formation of CuO nanoparticle. TEM image with respect to the nanoscale CuO was tested and result indicated that the morphology of CuO was approximately sphere and the diameter range from 7.5 to 12 nm. Thanks to the superior dispersing ability, this CuO nanofluid possessed a 30.4% receiver efficiency enhancement ratio compared with pristine water in the case of 0.25 *wt.*% nanofluid at the optimized depth of 1 cm.

Zamzamian et al. synthesized a Cu nanoparticle filled EG based nanofluid and studied its performance when using as a thermal collector [157]. Though numerous studies regarding the use of nanofluids into flat-plate solar collector, this work provided a new one-step, where a chemical hydrolysis was involved, to access highly stable Cu nanoparticle filled nanofluids. Aiming at obtaining a stable Cu nanoparticle, a copper precursor, $CuSO_4 \cdot 5H_2O$ was used to fully dissolve in base solvent, and the reduction process, which was induced by $NaH_2PO_2 \cdot H_2O$ in EG as the solvent. A similar work was done by Kumar et al. where a superior thermal conductivity, calculated to be 1.34 times over than base solvent, was found [158]. Glucose can work as a reductant under the same reaction environment as demonstrated by Shenoy et al [159]. Besides EG base solvent nanofluid, this one-step method for making copper nanofluid was also applicable in the case of water based nanofluids. For example, Khoshvaght-Aliabadi et al. produced a copper water nanofluid by using a one-step method, namely electro-exploded wire technique [160]. This nanofluid was subsequently subjected to experimental analysis on thermal-hydraulic performance in different plate fin channels. IL could be also used as a reaction medium as well as base solvent to prepare a nanofluid in a one-step chemical way. Zhang et al. fabricated a non-spherical gold IL nanofluid by adopting tannic acid as the reductant [161]. Mechanism study indicated that IL is of great importance for the whole reaction as it also acted as a synthetic template.

2.3.2 One step synthesis of solvent free nanofluid through a chemical way

Zheng et al. synthesized a solvent free nanofluid hybrid material which mainly consisted by MWCNTs and silica nanoparticle through a simple chemical compounded way [34]. In this work, 3-(trimethoxysilyl)-1-propanethiol was applied to modify silica nanoparticles because nanoparticles are prone to be flocculated and agglomerated without modification. The solvent-free hybrid nanofluids containing MWCNTs that decorated with silica nanoparticles were synthesized through PEO-*b*-PPO-*b*-PEO and carboxylic MWCNTs. Surface of MWCNTs was modified to carboxyl group to provide hydrophilicity. Experimental results revealed that those groups were quite necessary for MWCNTs to further integrate with other functional groups. In this work, MWCNTs/silica nanoparticle content can reach to 31 *wt.* % with keeping a liquid-like behavior in the absence of solvent at 45 ^{o}C. Notably, the solidification and melting process shows a promising reverse ability that it could be kept over many cycles without changing both phase transition temperature and latent heat which proved the highly stability of the as-prepared solvent-free nanofluid.

Besides MWCNTs, graphene could be also used in preparation of solvent-free nanofluid by modifying the structure of graphene. Graphene oxide/titanium dioxide (GO/TiO_2) solvent-free nanofluid was firstly synthesized by Zheng et al. by employing GO and TiO_2, which was *in-situ* deposited through a chemical hydrolysis process, as a core material, (3-glycidyloxypropyl) trime thoxysilane (KH560) and polyetheramine-M2070 as the shell material. The nanofluids displayed promising performance toward great fluidity, thermal stability and solubility in a series of organic solvents [162]. A novel multifunctional graphene/Fe_3O_4 filled nanofluid that displayed a low viscosity and liquid behavior at room temperature with GO@Fe_3O_4 as a core and sulfuric acid-tailed organosilaned as corona and polyether amine as canopy was also developed by Zheng et al [163]. The hybrid nanofluid displayed superaramagnetism with specific magnetization of 0.39 emu/g owing to existence of Fe_3O_4. Li and Zheng et al. reported a chemically MGE based solvent free nanofluid from tertiary amine and sulfonate anions (**Fig. 5a** and **5b**) [164]. The graphene content of the nanofluid was up to 12.05 *wt.* % and thickness of the MGE ranged from 2 to 5 nm. The conductivity performance of G-PEGs showed that the percolation threshold was around 0.99 *vol.* %. It should be noted that the G-PEGs featured a relative low viscosity at an ambient temperature (67.6 pa·s at 20 ^{o}C). Moreover, the G-PEGs displayed an excellent dispersing ability in several solvents, such as ethanol and water. These properties of G-PEGs offered some new technical and scientific chances for the further utilization of graphene. Further study revealed that the graphene based solvent-free nanofluid can be employed as lubricant as demonstrated by Zhang and Li et al [165]. GO was also capable to be used as a core to construct a solvent-free nanofluid. As demonstrated by Li and Zheng et al., a solvent-free GO nanoribbons colloids can be achieved by grating organosilanes and polyether amine (**Fig. 5c** and **5d**) [166]. Properties of the as-prepared nanofluids, such as mechanical, thermal and tribological were comprehensively studied. The obtained experimental results and the characteristic of this solvent-free nanofluid revealed that a green and facile approach to alleviate the friction coefficient of this kind of resin-based composite was realized.

Hybrid nanofluid, synthesized from a composite core of poly(2-dimethylamino ethyl methacrylate) microgel and silica (PDMAEMA/SiO_2) and a shell of polyetheramine (M2070), was reported by Yao et al. *via* a sequential inversed emulsion polymerization, biomimetic solidification and grafting approach (**Fig. 5e** and **5f**) [167]. CO_2 adsorption performance of these nanofluids was studied under a series of CO_2 pressure ranging from 0.5 MPa to 4.5 MPa at 25 °C. These results revealed that nanofluid with a walnut core/shell structure showed a much enhanced CO_2 adsorption capacity compared with that of solid spherical one. Importantly, this type of nanofluids displayed an excellent stability that it could be kept almost unchanged over ten adsorption-desorption cycles.

Zheng et al. prepared a series of core/shell organic/inorganic hybrid nanoparticle materials by using MWCNTs and silicon SiO_2 as the core materials [168]. The as-prepared material displayed a liquid state without adding water at ambient temperature, further study revealed that those kinds of materials can be categorized into three types, namely, the power strip model, the collapse model and the critical model, upon the weight ratio of the two components in the core. CO_2 absorption ability was used to evaluate the performance of the as-prepared nanofluids, and the study indicated that nanofluids with the power strip model showed the optimized adsorption capacity for CO_2 probably owing to capacity for the reaction with CO_2 derived from its low viscosity and active groups.

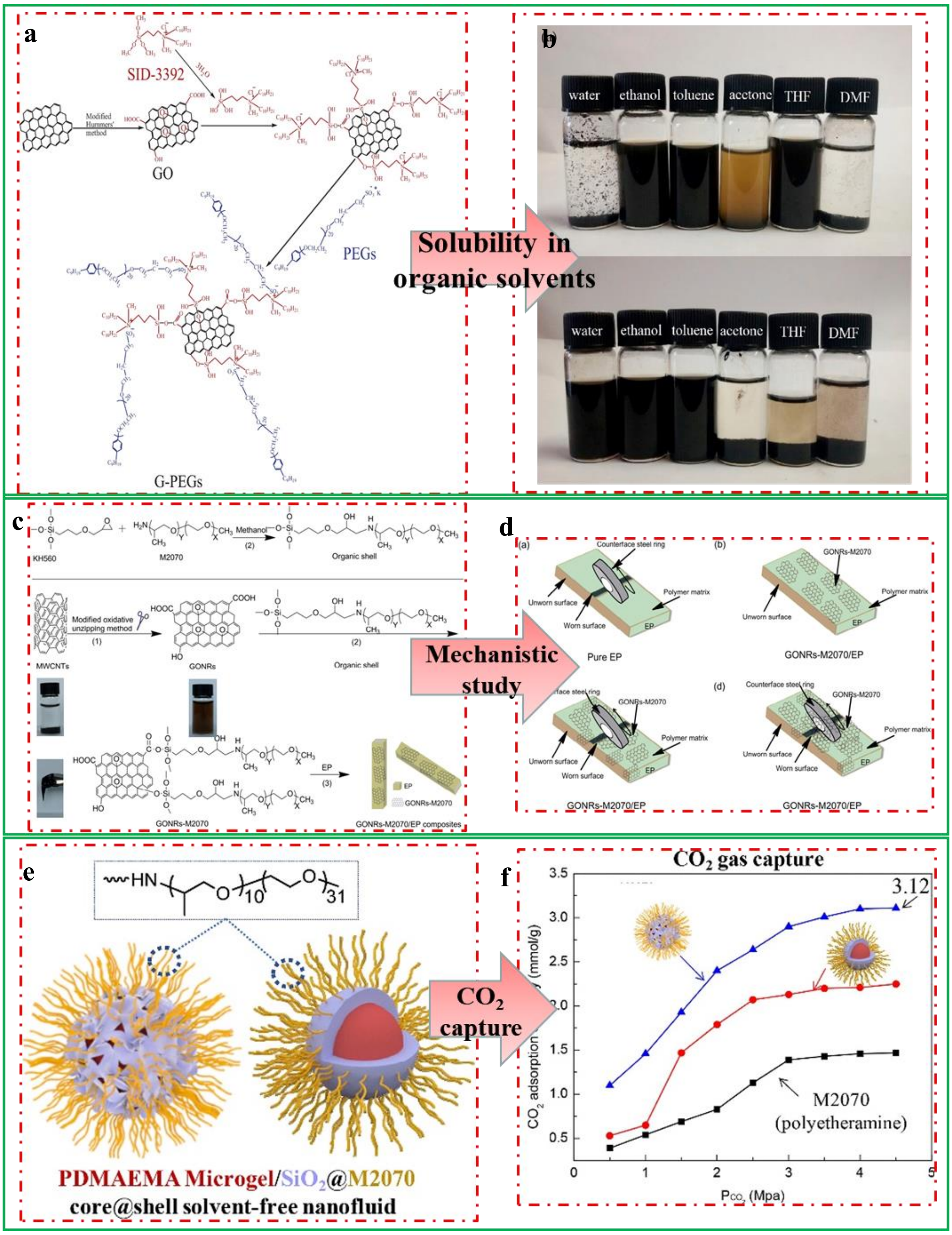


Fig.5 (a) Reaction scheme of the liquid-like graphene nanofluids (b)Solubility of G-SID and the solvent-free graphene nanofluid (c) Schematic diagram of steps for the synthesis of a solvent-free GO nanoribbons colloids (GONRS-M2070) and GONRs-M2070/ epoxy resin (EP) composites (d) A schematic representation of wear mechanism of the GONRs-M2070/EP composites. (e) Expansion of poly(2-dimethylamino ethyl methacrylate) microgel and silica (PDMAEMA/SiO_2)

nanofluids and their magnification (inset) and contraction of PDMAEMA/SiO_2 nanofluids.(f) carbon dioxide adsorption properties of Walnut core structures for nanofluids. (**Fig. 5a** and **5b** were reproduced with permission from ref. [164], Copyright (2014) Elsevier) (**Fig. 5c** and **5d** were reproduced with permission from ref.[166], Copyright (2016) Elsevier) (**Fig. 5e** and **5f** were reproduced with permission from ref.[167], Copyright (2019) Elsevier)

Fabrication MWCNTs with polyether amine canopy structure enabled a liquid like solvent-free nanofluid reported by Li and Zheng et al [168, 169]. The unprotonated amine part concentration has a great influence on CO_2 uptake ability. Meanwhile, the lower melting point and viscosity of this MWCNTs based solvent free facilitated a promising CO_2 absorption efficiency. It should be noted that this work provided an evidence that the as-obtained solvent-free nanofluid displayed exciting CO_2 capture capacities compared to that of corresponding pristine polyether amine and MWCNTs, which clearly showed the merits of the solvent-free MWCNTs nanofluids. Additionally, some typical examples were summarized in table 5.

Table 5. One-step synthesis of stable polymer aided nanofluids.

Corona and canopy	Nanoparticles	Applications	Ref.
Organosilanes (KH560) and polyether amine (M2070)	GO nanoribbon	Enhanced mechanical, thermal and tribological performance	[166]
Ionically tethered polyether amine terminated polymers	MCNTs	Carbon dioxide uptake	[169]
Hyperbranched	Graphene	Lubricants	[165]

polyamine-ester			
Tertiary amine and sulfonate anions	Graphene	--	[164]
Sulfuric acid-terminated organosilanes and polyether amine	Graphene@Fe_3O_4	--	[163]
KH560 and M2070	MWCNTs/SiO_2	Carbon dioxide uptake	[168]
KH560 and M2070	SiO_2	Carbon dioxide uptake	[167]

3. Nanofluid utilized in micro/nano scale energy transportation

Owing to this unique characteristic which derived from Brownian motion and nanoscale effect of nanofliller, endows nanofluids with advantageous heat and mass transfer properties, and utilization in nano/micro heat exchangers. Especially in the heat exchanger, which recognized to be a classical energy transportation field, nanofluids play a key role, and a predominate researcher, Khanlari, has made a series of contribution in this aspect.[170-173] whereas, applying nanofluids to absorb gas, liquid or solid pollutants from the point of view of environment protection, adjusting the chemical reaction proceedings through the regulation of reaction temperature or acting as a catalyst to promote organic chemical reactions etc. in which energy transportation is the dominate factor and also belongs to the energy related application field that should be considered since nanofluids were able to play a key role in those processes, were concerned by few people so far. Out of this consideration, this review aims to summarize the recent advances in utilization of nanofluids in a chemical related micro/nano energy transportation way, to make a supplementary for a vast of reviews with respect to nanofluids using in thermal related fields.

3.1 Nanofluids used as catalysts to promote organic reactions

Nanofluids are mainly consisted of a dispersed nanometer scale solid particle and a base solvent. Because nanofluids exhibit high thermal conductivity and high stability, they have been widely used in the field of thermal management and energy storage [174-177]. Investigation relating their applications in chemical production or chemical transformation is not widely seen. In the meantime, catalysis, especially for heterogeneous catalysis, has a predominant role in chemical reactions for the production of bulk and fine chemicals in industry and academia as it is recyclable after the reaction [178-180]. Among heterogeneous catalysis, nanoscale based catalyst has been paid much research attention due to its unique chemical, physical, optic, and mechanic properties derived from the special nano-size effect. Combining the advantageous of nanofluids and heterogeneous catalysis might be an interesting topic in terms of reaction efficiency and environmental considerations and provide new inspirations for advancing novel chemical diversity [181, 182]. It is also rational to predict that nanofluids may be applicable in realizing heterogeneous catalysis due to their similar working component [183, 184]. Moreover, owing to the superior stability of nanofluids, they also provided an efficient pathway to facilitate the heterogeneous catalysis in microreactors, especially in a flow reaction system. For example, Su et al. demonstrated a heterogeneous catalysis in microreactors by the means of nanofluids for the production of fine chemicals (**Fig. 6a,6b** and **6c**) [35]. In this work, a heterogeneous catalyst which fabricated from immobilization of $FeCl_3$ catalyst on a nanoscale SiO_2 was synthesized and applied into the preparation of benzyl chloride nanofluids. In order to achieve a high stability, dispersant sodiumdodecylbenzenesulfonate (SDBS) was used along with the nanoparticle. Experimental results revealed that the reaction was proceeded smoothly in a micro-reactor based flow system towards the benzylation of toluene with benzyl chloride for the synthesis of monobenzyl toluene and dibenzyl toluene. Notably, the nanofluids catalyst can be reused for at least three times with keeping its comparable reactivity. It should be mentioned that this study paved a pathway for realizing the utilization of nanofluids in micro reactor.

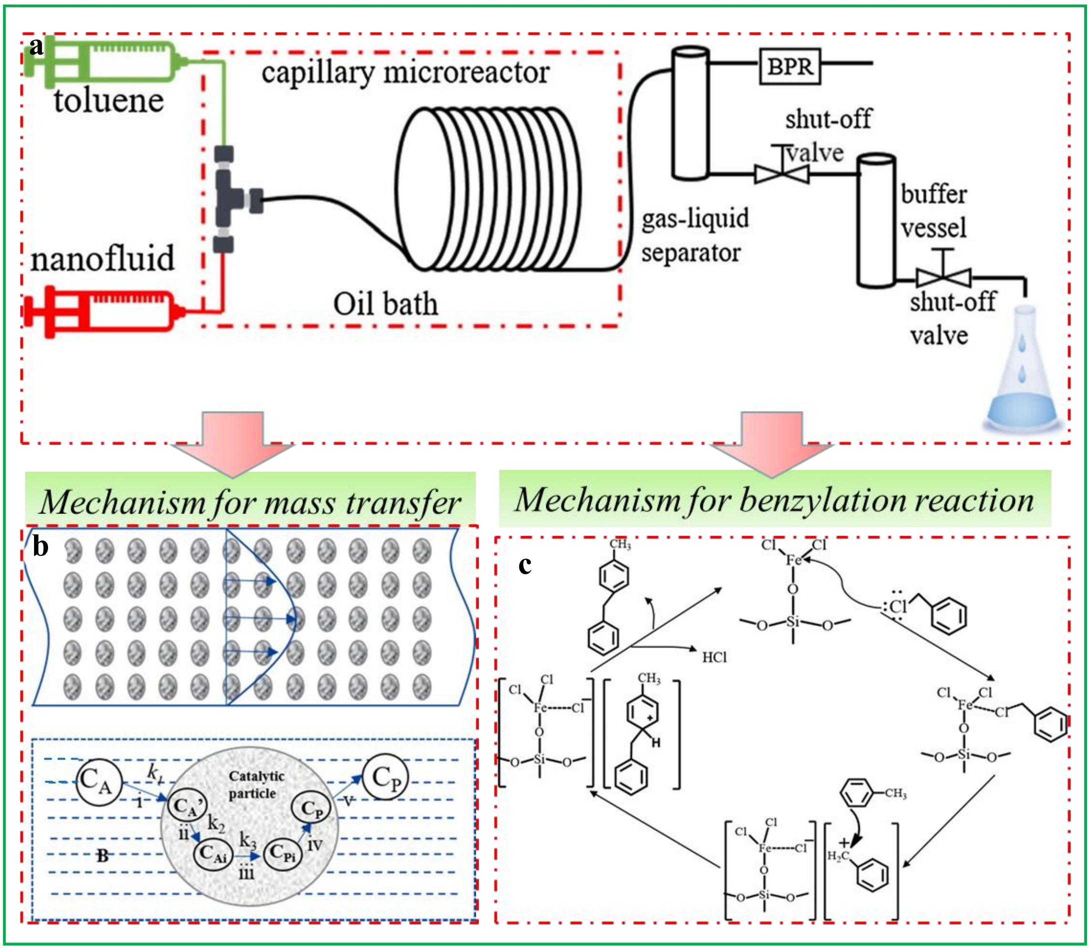


Fig.6 (a) Schematic overview of the experimental apparatus. (b) Schematic diagram of nanofluids in a capillary microreactorc. (c) The mechanism of alkylation between toluene and benzyl chloride. (**Fig.6a,6b** and **6c** were reproduced with permission from ref. [35], Copyright (2018) Elsevier)

In addition, Tamaddon et al. used ZnO filled nanofluids as dual media and efficient catalyst for chemo-selective amidation aliphatic carboxylic acid [185]. ZnO oxide is a versatile metal oxide which has been adopted as a catalyst in a series of organic reactions. It has a low price and environmentally friendly. Moreover, its high capacity, high heat conductivity and low thermal expansion make it as a good candidate for using in preparation of nanofluids. Besides, amides are of great importance when used as building blocks in the synthesis of several drugs, peptides, polymers and agrochemicals. In this work, nanofluids, made from ZnO nanoparticles and glycerol base solvent was used as both catalyst and reaction medium. Other kinds of metal oxides, including TiO_2, MgO, Al_2O_3 were tested upon the construction of amides, among them, ZnO quite stood out that afford the desired product in optimized yield. This ZnO glycerol nanofluid system was also proven to be applicable for a broad substrate scope that carboxylic acid bearing varies substituents could participate in the reaction in good and excellent yields, which offered considerable merits in terms of simplicity, availability for scale up, low environmental and economic burden and excellent chemoselectivity.

Methanol reforming is a promising route for the production of hydrogen since it was a low cost and less toxicity resource and easy to store. Generally, catalysts for methanol reformation was found to be copper or noble-metals, among them, copper-based catalyst is favorable due to the relative low price, however, the reforming temperature reaction temperature of methanol to hydrogen is up to 200-300 °C, hence, a large amount of external energy input is needed. Xuan et al. proposed a CuO/ZnO composite filled nanofluid, which could act both a reaction catalyst for methanol reforming reaction and solar harvesting medium to fulfill the temperature requirement, thus the external heating could be omitted [186, 187]. Experiment results revealed that the maximum temperature of the nanofluids could reach to 72.649 °C with the volume fraction of 0.01%, and the photothermal efficiency was up to 97.3% at 30 °C.

Besides metal oxide nanofluid, metal nanofluid which prepared from a reduction method was also reported to be capable of using in catalysis. For example, Moumen et al. synthesized a palladium nanoparticle using a polyol assited-microwave process in a few minutes [188]. The synthesis of nanofluids mainly relied on the reduction of metal salt in an EG medium in the presence of a copolymer which employed as both reductant and stabilizer. Microscopy analysis revealed that the nanoparticle was distributed in a narrow diameter range. Notably, this stable palladium was proven to be highly efficient towards Suzuki-Miyaura reaction, Heck reaction and Sonogashiya reaction, which clearly demonstrated the feasibility of nanofluids in terms of catalysis. Furthermore, Yue et al. prepared three different kinds of palladium nanoparticle catalysts with the modification of octadecanethiol, octadecylamine and both [189]. Highly stable palladium nanoparticle filled nanofluids was prepared by dispersing three different kinds of palladium in decalin and kerosene. Pyrolysis of decalin-based nanofuids experiment indicated that the palladium filled nanofluids displayed good stability which derived from the combined effects of palladium and its ligands. Li et al. prepared a series of gold nanoparticle filled nanofluids with the aid of a several of surfactants, such as *N*,*N*-dimethylhexadecylamine and butanediyl-1,4-bis(dimethylcetyl ammonium bromide) [190], The as-prepared hydrophobic gold nanoparticle exhibited superior stability in non-polar solvent. It should be mentioned that this high stable nanofluid offered a superior catalytic activity for cracking of tricycle decane over the thermal cracking.

3.2 Nanofluids used as gas absorption mediums

Gas pollution has become a critical problem for the current trend of sustainable economic and industrial development. Greenhouse gases in the atmosphere are important components of gas pollution resulted by a rapid increasing of industrial development. Thus, greenhouse gas capture from industrial gas stream by using efficient and economic devise is of great significance. Nanofluids have been subjected to study in various application occasions with the purpose of improving the heat and mass transfer efficiency [191, 192]. Numerous reports concerning the mass transfer enhancement of nanofluid were seen in literatures, in the meantime, owing to the superior mass transfer performance, nanofluids were also demonstrated to be capable of using in gas absorption field, especially for using as CO_2 absorbents. For example, Rezakazemi et al. reported water based nanofluids by filling CNT and SiO_2 with a hollow fiber membrane contactor by using a numerical simulation method [193]. The study showed that the absorption rate could reach to 16% by introduction of 0.05 *wt.* % of SiO_2 nanoparticle, CNTs displayed a much higher adsorption efficiency that could achieve to 34% for the same mass fraction of CNTs nanofluids. Keshavarz et al. studied SiO_2 and CNTs nanoparticle filled water based nanofluids for CO_2 absorption in an experimental way, it was found that CNTs showed a much better separation performance than that of SiO_2 and CO_2, and the gas absorption efficiency decreased slightly with the increasing CO_2 inlet concentration probably due to the saturation of the fluids [194]. Keshavarz et al. gave a comprehensive study on CO_2 absorption performance of DW based Fe_3O_4, CNT, SiO_2, and Al_2O_3 filled nanofluids [32]. A pilot-scaled hollow fiber membrane was installed to study the gas-liquid separation efficiency. The results showed that some parameters, including, gas flowing rate, liquid flowing rate, concentration of inlet CO_2 and the nanoparticle concentration could heavily affect the CO_2 absorption efficiency. The utmost absorption rate enhancements for different nanoparticle filled nanofluids are 43.8% at 0.15 *wt.* % Fe_3O_4, 38.0% at 0.1 *wt.* % CNT, 25.9% at 0.05 *wt.* % SiO_2, and 3.0% at 0.05 *wt.* % Al_2O_3 respectively compared with their corresponding base solvent. Besides water based nanofluids, Keshavarz et al. also studied amine solution based nanofluids for its CO_2

absorption performance by using SiO_2, Al_2O_3, CNT, and Fe_3O_4 nanoparticles as nanofillers (**Fig. 7a** and **7b**) [195].

Kang et al. not only studied the absorption efficiency and mechanism of SiO_2 and Al_2O_3 nanofluids, but regeneration of the nanofluids after CO_2 absorption was also studied that Al_2O_3 exhibited both superior up taking and regeneration performance over SiO_2, which were quite in line with their previous research results (**Fig. 7c** and **7d**) [196, 197]. To further understand the mechanism behind CO_2 absorption performance efficiency, research regarding the CO_2 regeneration system was studied by using a visualized platform that the surface effect between nanoparticle and CO_2 was heavily affected the working performance of the nanofluids [198].

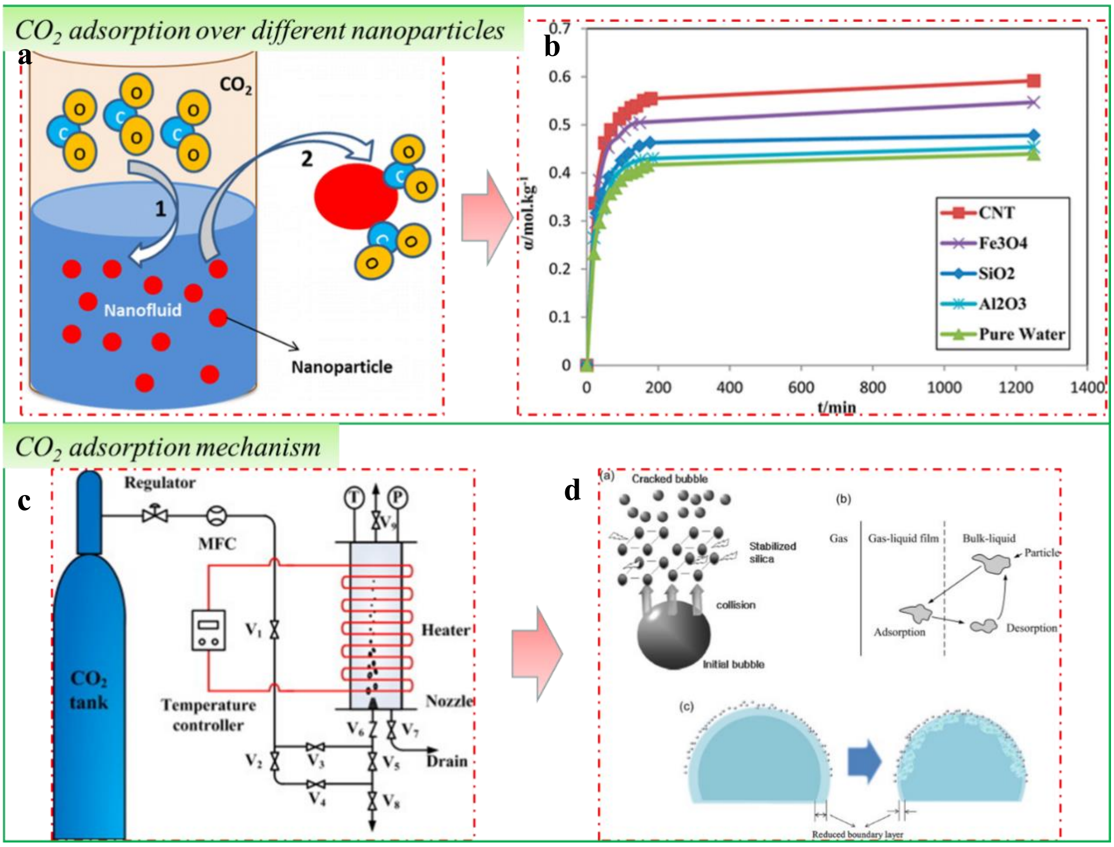


Fig.7 (a) the scheme of nanofluid absorb CO_2 (b) At the concentration of 0.02 wt %, pressure of 40 bar and temperature of 308 K, the absorption of carbon dioxide by SiO_2, Al_2O_3, Fe_3O_4 and CNT nanofluids. (c) Novel Silica Filled DES Based Nanofluids for Energy Transportation. (d) Absorption mechanism of nanofluids (**Fig.7a** and **7b** were reproduced with permission from ref. [195], 2015 American Chemical Society) (**Fig.7c** and **7d** were reproduced with permission from ref.[197], 2017

American Chemical Society)

Kang et al. developed nanofluids with the addition of Al_2O_3 and SiO_2 nanoparticles in methanol base solvent for CO_2 absorption in a tray column absorber through an experimental method [199]. The results indicated that the absorption enhancements for Al_2O_3 and SiO_2 were 9.4% and 9.7% respectively compared with pristine methanol. The author pointed out that SiO_2 gave a better performance than that of Al_2O_3 from the point of view of absorption ability. Mass transfer characteristics during CO_2 bubble absorption and diffusion process in nanofluid with Al_2O_3 nanoparticle, the surface tension and viscosity of the nanofluids were also investigated to know CO_2 absorption performance by the same group [196]. Haghtalab et al. studied CO_2 absorption in SiO_2 and ZnO filled water based nanofluid, it was found that the enhancement of CO_2 solubility in ZnO water nanofluid over SiO_2 water nanofluid and pure water. Moreover, the mechanism responsible for the CO_2 absorption enhancement for this nanofluids was presented in this work [200]. Lu et al. also experimentally demonstrated the effect of nano-particles on CO_2 absorption in a stirred thermostatic reactor by using Al_2O_3 and carbon nanotube particle and studied the surface effect on CO_2 absorption performance [201].

Mohebbi et al. proposed an amine-based nanofluid with the aim at simultaneously absorbing of CO_2 and H_2S from a $CO_2/H_2S/CH_4$ gas mixture by filling with nanoscale Al_2O_3 [202]. A wetted wall column system in a laboratory was employed to study the gas absorption efficiency. The results showed that CO_2 absorption efficiency could get a 33% improvement at 0.05 *wt.* % of Al_2O_3/amine-based nanofluids, and also 40% at 0.05 *wt.* % of SiO_2/amine-based nanofluids. The basic solvent, piperazine, was also proven to be efficient for CO_2 absorption by combining nano heavy metal oxide particles, TiO_2, ZnO and ZrO, as demonstrated by Ghaemi et al [203]. In this work, a continuous stirrer bubble column was set up for CO_2 passing through the platform, the research results revealed that some process parameter, such as nanoparticle type, solid loading and stirring speed played important roles for CO_2 capturing. Interestingly, the author found that the absorption performance of the nanofluids went up when the stirring speed was lower than 200 rpm, while, it became worse when a higher stirring speed was tested. In addition, methyldiethanolamine, another amine type base solvent, was also reported to be an efficient nanofluid base solvent for CO_2 absorption by blending with polyethyleneimine functionalized copper nanoparticle [204]. Moreover, Sun et al. studied CO_2 absorption in an aqueous amine solution based nanofluid by using a 3D unsteady model, and found that the mass transfer model was feasible towards the prediction of the experimental results reliability [205].

Darvanjooghi et al. prepared a Fe_3O_4/water nanofluid under the impact of AC and DC magnetic fields [206]. The coated Fe_3O_4 nanoparticle were prepared through a co-precipitation method, some characterization indicated that the nanoparticle surfaces were uniformly coated with hydroxyl groups, thus a good affinity in water solvent could be expected. In addition, the experimental results demonstrated that mass diffusivity of CO_2 in nanofluid increased when the intensity of the magnetic field increased and the diffusion layer thickness was thus decreased. Esfahany et al. studied the nanofluids with respect to their utilization in a biogas, H_2S, absorption. Oxygen group functionalities and silanol group was attached on GO and synthesized silica respectively with the aim to enhance their absorption ability [207]. It should be mentioned that GO/water nanofluid could absorb H_2S while CO_2 absorption was diminished to zero when the nanoparticle concentration higher than 0.02 *wt.* % owing to the oxygen groups attraction effect on GO surface.

3.3 Nanofluids used as electrolytes

As it is well known, research regarding the nanofluids was initiated aiming at solving the poor thermal conductivity of single-phase working fluids. Numerous references revealed that the ionic conductivity enhancement mechanism was in fact similar to heat conductivity in nanofluids. In the meantime, a main obstacle for the increase of the energy density of cell was relying on the working voltage. While, the cell voltage was heavily associated by the chemical stability of the electrolyte because a higher voltage would inevitably result in decomposition of electrolyte caused by the production of a large amount of Joule heat owing to its relatively poor electrical conductivity. Therefore, from the point of view of improving cell density, a nanofluid based electrolyte will be an important alternative for traditionally used single phase electrolyte. The study upon the using nanofluid in electrolyte has been frequently in literatures. For example, Qian et al. reported a 4 V supercapacitor by using an $EMIBF_4$-SWCNT nanofluid electrolyte with the purpose to increase the capacitance of the supercapacitor [208]. At a scan rate of 200 mV s^{-1}, the capacitance performances of the electrode in different electrolytes were studied, the results indicated that the supercapacitor has a gross improved capacitance performance owing to the participation of nanoscale MWCNTs. The effect of SWCNTs in ILs on the cycling stability was tested at 4V and a scan rate of 200 mV^{-1} for 4000 cycles, which clearly demonstrated the superior stability of this nanofluid based electrolyte. The author also expanded the nanofluid electrolyte into a 5V supercapacitor system to enhance the energy density, capacitance and broaden the power density of electrode. The cycling experiment suggested that the cycling stability was greatly improved due to the decrease of bulk phase resistance of IL (**Fig.8a** and **8b**)[209]. Additionally, mass transfer phenomena in nanofluids, which composed by nanoscale Al_2O_3 and base electrolyte was studied by Wilk et al (**Fig.8c** and **8d**) [210]. The experimental results revealed that the mass transfer ratio was not proportional to the increase in particle fraction and the mass transfer coefficients achieved the lowest values at the largest value of particle fraction by using the electrochemical limiting current technique.

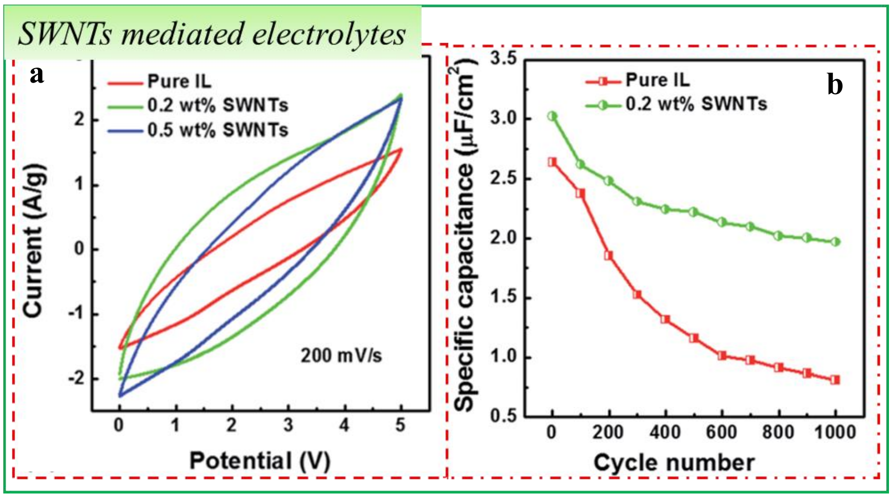


Fig.8 (a) The capacitive properties of the supercapacitor (SCs) with pure IL and different nanofluids as electrolytes. SCs CV curve at a high scanning rate of 100 mV/ s and 200mV/s (b) cycling stability of different SCs under 5 V at the scan rate of 100 mV s^{-1}. (**Fig. 8a** and **8b** were reproduced with permission from ref.[209], Copyright (2015) Elsevier)

Devaraj et al. studied the capacitance enhancement in the supercapacitor by using SiO_x nanofluid based electrolyte [211]. The capacitance properties of $MnCO_3$ were studied in 0.1 M $Mg(ClO_4)_2$ electrolyte in the presence of SiO_x nanofluid in electrolyte. The study suggested that the addition of small amount of SiO_2 nanofluid in the electrolyte provided a higher diffusivity and a more conductive route. Also, the nanofluid containing electrolyte was quite stable that it can be kept over a month without precipitation.

Besides using in supercapacitor, nanofluids based electrolyte can be applied in a lithium metal battery. For example, Bhattacharya et al. incorporated IL functionalized TiO_2 nanoparticle with low conductive 0.6 M lithium salt doped *N*-methyl-*N*-butylpyrrolidinium bis(trifluoromethylsulfonyl)limide IL electrolyte with the aim to improve the ionic conductivity and the lithium transference number in electrolyte [212]. It was found that the Li/$LiMn_2O_4$ cell with IL based nanofluids electrolyte delivered a discharge capacity of about 131 mAh/g at 25 °C, which was significantly higher than that of conventional 0.2 M Li salt dissociated Pyr(14)TFSI electrolyte. The outstanding capacity retention performance of the cell as compared to conventionally used one clearly indicated that the great application potentiality of this optimized novel electrolyte for safer and environmental benign lithium batteries. MWCNTs was applicable to disperse in electrolytes to improve the energy storage capacity of vanadium redox flow battery reported by Park et al [213]. In this work, nanofluids with different mass fraction of MWCNTs were tested and compared with the pristine electrolytes. Gómez-Romero et al. applied a $LiFePO_4$/rGO aqueous nanofluid into battery and supercapacitor material in flow cells [214]. In this work, a battery material and a supercapacitor material in form of nanoparticle dispersed in an aqueous electrolyte to evaluate the electrochemical activity of this electroactive nanofluids. Effective application of dispersed electroactive particles was demonstrated, which turned out to be superior to the same $LiFePO_4$ materials. This research paved a way for the possible application of electroactive nanofluid electrodes in an alternative flow battery. Moreover, Feng et al. studied the electrical conductivity and diffusion behavior of ferro/ferricyanide-electrolyte-based alumina filled water-based nanofluids [215]. The author demonstrated the stable alumina nanofluid which prepared using a sequential stirred bead milling method and tested its electrical conductivity that can be up to 2420 muS/cm at 23 °C. Owing to the considerable high electrical conductivity and stability, the nanofluids were deemed to possessing the potential to be used in a thermo-galvanic application.

3.4 Nanofluids used as temperature regulation mediums to control the reaction process

Besides working as a thermal conductive medium for thermal energy transferring and management, nanofluids can be adopted in some other temperature regulation fields. Process intensification, firstly termed in the 1980s, composed varies approaches leading to chemical process in a small footprint which featured by inherently safe, reduce or eliminate the need for toxic compounds and energy efficient. The principle of intensification is reducing the length and length scales of reaction platform where mass and heat transfer might happen. One of the possibilities in increasing the total efficiency of process intensification are relying on improving the heat transfer efficiency of the micro-exchangers. Among them, modification of the surface of fluid flow system and enhancement the thermal conductivity of the fluid itself are the main two solutions. Nanofluids, possessing a superior thermal conductivity could be an ideal choice for heat transferring medium. For example, Lapkin et al. applied nanofluids in process intensification for the reduction of benzaldehyde (**Fig. 9**) [216]. In this work, TiO_2 material was dispersed in ethylene glycerol to form nanofluids to study an integrated reactor-heat exchanger. Experimental results indicated that a 35% increase in the overall heat transfer coefficient was obtained under a steady and continuous experimental condition. Moreover, the nanofluids afforded a very rapid response for the reaction of an aromatic aldehyde with molecular hydrogen under dynamic reaction control through prompt temperature regulation.

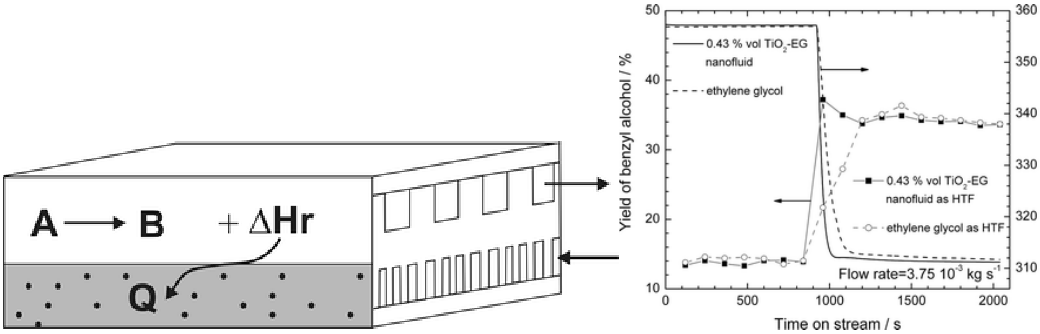


Fig.9 Experimental rig for heat transfer and hydrogenation of benzaldehyde experiments and the benzyl alcohol concentration in the outlet of the reactor as a function of the reaction temperature. (Reproduced with permission from ref. [216], Copyright (2018) Royal Society of Chemistry)

4 Conclusion and outlook

Since the unearthing of nanofluids, numerous reports, relating their preparation methodologies, analysis approach, real application for heat and mass transfer intensification, and heat transfer mechanism were widely found [217, 218]. In the meantime, chemistry is one of the most basic subjects to study the matter formation and constituents. This paper is aim at summarizing the nanofluids preparation process in which a chemical transformation was involved and application scope of nanofluids in energy transportation related fields. For the preparation of nanofluids in terms of chemical approach, nanoparticle formation in a chemical way, base solvent production in a chemical way and synthesizing nanofluids in a chemical one-step way were included. The application of nanofluids in some unsummarized energy transportation fields, such as catalysis in organic reactions, gas absorption, electrolyte and temperature regulator medium were comprehensively discussed. This paper will ambiguously provide a refence for the people who wants to developed a desired nanofluid with a specific function. Anyway, the utilization of nanofluids in some other uncommon occasions would beneficial for people knowing the energy transportation and harvesting insight and thus further broadening the utilization scope of nanofluids, especially in materials synthesis, carbon emission decreasing and renewable energy storage and transportation fields.

Though nanofluids have been showing vastly exciting potential application, hinders before their commercialization are still existed. To accelerate the pace for advancing of nanofluids, the following issues should be paid more efforts in the future:

1. Mechanism responsible for the thermal conductivity enhancement should be paid more attention.

So far, many models and theoretical formulas were launched to predict or verify the experiment results, however, an agreement between experiment results and theoretical is still lack to some degree [219, 220]. Additionally, experiments result from different groups sometimes are not inconsistent. So, to make a relatively uniform principle to study the behavior of nanofluids in a more scientific way, it is important to find more influence factors that dominate the performance of nanofluids.

2. Stability of nanofluids is a crucial issue for both practical utilization and scientific research.

Because of the heterogeneous state of nanofluids and density difference between nanofillers and base solvent, the aggregation and sedimentation of nanoparticles are inevitable. For the long-term stability, and the stability in a practical condition, and the stability after thermal cycles should be paid more attention because it will cause the clogging of flow system in a real application system. Adding a dispersant is a common approach to solve this problem, however, the decomposition and aging of dispersant will result in a negative effect in the case of complicated application conditions and long-term stability. Permanent modification of nanoparticle in a chemical methodology to enhance the affinity of nanofillers and base solvents should be a more efficient way to increase the stability inherently.

3. The investigation of the thermal performance of nanofluids at a wide temperature range is insufficient.

Study the nanofluids application at a wide temperature range may widen the possible application scope, such as in high temperature solar energy absorption, high temperature energy storage and low temperature thermal management[221]. In this case, base solvents play a crucial role to fulfil the requirements. Traditionally, IL is a promising choice owing to its wide liquid range and less volatile, however, it also suffers from high costly, sophisticated preparation procedure and safety uncertainty. So, a more environmentally benign and less costly alternative would be more promising. Meanwhile, facilities that could be applied in high temperature analysis are needed to be further improved. Moreover, the high temperature will accelerate the decomposition of dispersant used for the stabilization of nanofluids that should be further considered.

4. Flow drag reduction of nanofluids is crucial for practical application.

Viscosity rising with the increasing fraction of nanofillers is an important drawback because it associates with the pumping power. Increasing the compatibility between nanofillers and the base fluids through modification of the interface properties of the two phases should be a feasible approach to address the flaws [222]. Besides, the effect of microscope morphology of nanofillers needed to be considered in terms of drag reduction in various shape flow systems.

5. Nanofluids recycle is a topic that should be paid more attention.

Recycle nanofluids could not only significantly reduce the material consumption, in particular for nanofillers, but also avoid the secondary pollution caused by the nanoparticles. However, the separation of nanoparticle from the base solvent is still a main bottleneck because it is somehow a kind of contradictory to the stability of suspension. To facilitate the recyclability, external field, such as magnetic, electricity and force were usually used in the specific nanoparticle cases. For example, He et al. synthesized the recyclable Fe_3O_4@TiO_2 and Fe_3O_4@CNT for photo-thermal conversion system [223, 224]. Due to the presence of magnetic component, these types of nanoparticles could be facilely recovered from the nanofluids, and the recovery rate and efficiency could be controlled by adjusting the external magnetic field strength and direction. Therefore, nanofillers with specific properties in a chemical modification approach provide more chance for recycling nanofluids in a facile way.

6. Nanofluids in micro/nano scale applications have great potential to be further explored.

Though nanofluids are well recognized to be enhanced thermal conductivity and some unique properties owing to the contribution of nanofillers, the application of nanofluids in energy transportation, especially in some related micro/nano scale energy transportation was heavily hindered by the abovementioned shortcomings. On the other hand, as the continuous size shrinkage of electric devises and the raising power input, highly efficient micro/nano scale energy transportation and transfer is at the core of scientific research and engineering applications. As a novel working fluid, nanofluid will ambiguous attract ample attention and visibility, we hope this review paper can help people to understand nanofluids in terms of either the preparation or application scope.

Acknowledgements

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