Long-term Stability of Graphene Based Nanofluids

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Abstract—Long-term stability of nanofluids remains quite challenging for graphene-based nanofluid preparation. This is however a crucial aspect for their use in heat transfer applications. In this study, we have used the derived Hummers' method for graphene oxide preparation. Then, reduction of graphene oxide is realized in various conditions. Stability of nanofluids of graphene oxide and reduced graphene oxide are investigated. We show graphene oxide nanofluids suffer of rapid destabilization which dramatically reduces the thermal properties. Nanofluids prepared with reduced graphene oxide show an improved stability depending of the reduction conditions. NaBH₄ is recommended compared to N₂H₄ for which impurities are introduced in the graphene structure and destabilization easily occurs.

Index Terms—graphene, nanofluids, chemical reduction, long-term stability, heat transfer

I. INTRODUCTION

Heat exchange and evacuation is currently a major concern in development of new technologies in particular in electronics and more generally for energy conversion including renewable energies. Nanofluids have been proven to have the potential to drastically increase heat exchange compared to conventional fluids [1,2]. They are prepared by dispersing nanoparticles in a liquid medium in order to increase their properties. Carbon nanomaterials such as diamond, carbon nanotubes and more recently graphene that combine lightness, chemical stability and high conductivity are incontestably recognized to be the best candidates for the new generation of nanofluids [3,4]. Unfortunately, graphene is highly hydrophobic leading to a high tendency to agglomerate in the majority of solvent, in particular water [5]. Stability issue is the major roadblock for achieving control and precisely varying the relevant parameters for graphene nanofluid preparation. Among the graphene synthesis methods, graphene oxide (GO) prepared from graphite by the Hummers' method [6] allows low cost and large amount preparation of graphene. Even if a lot of defects are introduced in the graphene structure during

the chemical exfoliation, GO is often reported to have the advantage to be easily dispersed in water thanks to the introduced functional groups increasing the hydrophilic character of graphene sheets [7]. Unfortunately, disruption of the sp² bonding network in GO due to graphite structure damaging upon the Hummers' method and weak stability of GO nanofluids often leads to disappointing results. Reduction of GO to prepare reduced graphene oxide (rGO) has the advantage to restore the graphene structure, the chemical reduction decreasing hydrophilicity has to be well controlled to guarantee long-term stability of rGO-based nanofluids.

In the present work, we perform a critical analysis of the long-term stability of GO and rGO nanofluids. Chemical reduction of GO is performed with N_2H_4 and NaBH₄. GO nanofluids show a gradual reduction of their thermal properties due to destabilization. rGO nanofluids have an improved stability depending of the reduction conditions; NaBH₄ being a better reduction agent than N_2H_4 for which destabilization occurs.

II. EXPERIMENTAL

Graphite powder (SFG6 Primary Synthetic Graphite) of high crystalline quality was purchased from TIMCAL. GO was prepared from the derived Hummers' method. Typically, 2.5 g of graphite is mixed with 1.9 g of NaNO₃ (Sigma Aldrich). 85 mL of sulfuric acid (Sigma Aldrich) and 12.5 g of potassium permanganate (VWR Chemicals) are added under stirring while maintaining temperature below 20 °C. After 2 h at 35 °C, 125 mL of deionized water are slowly added to the above solution and followed by the addition of 10 mL of oxygenated water. After several cycles of rinsing-decantation with 10 vol. % hydrochloric acid and water, GO is ready to use. Intentionally, in order to avoid any additives, no pH modification was done in this study.

For preparation of reduced GO (rGO), 2 different reductive agents were used: i) sodium borohydride (NaBH₄) and hydrazine (N₂H₄). The relative concentrations of GO and the reductive agents vary so that the degree of reduction reaction is different for each sample. The pH of the solutions of GO ranges between 2 and 4.

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The solutions are allowed to settle without shaking for weeks, the aspect of the solutions is checked by eyes. Transmission Electron Microscopy (TEM) was performed using a JEOL ARM 200F cold FEG apparatus at an operating voltage of 80 kV. Scanning electron microscopy (SEM) observations were carried out using an XL30 S-FEG apparatus using Ultra High Resolution (UHR) mode. For the observations, a drop of the solution of GO or rGO is deposited on a holey carbon grid (200 mesh size), or directly on a sample holder for TEM and SEM respectively. Thermal conductivity measurements of the graphene-based nanofluids was carried out from the transient hot wire (THW) method. We used a KD2 Pro thermal property analyzer (Decagon Devices Inc.) equipped with a KS-1 probe. The experimental set-up for thermal conductivity measurements was described in ref. 8. Its accuracy was evaluated with distillated water within the temperature range of 10-50 °C, leading to a maximum standard deviation of 3.5 %. Before measuring thermal conductivity, both the sample and the probe were maintained at the required temperature during 15 min. Then, measurements were recorded every fifteen minutes as recommended by the manufacturer of the thermal conductivity device.

III. RESULTS AND DISCUSSION

As expected, GO and rGO appear as quite similar particles under electronic microscopy since their morphologic parameters are not modified by the chemical reduction; reduction indeed occurs under quite gentle conditions with both NaBH₄ and N₂H₄ used as reductive agent. GO and rGO are thin platelets of 2-10 layers and their side length reaches several micrometers (Fig. 1).



Figure 1 Typical images of electronic microscopy of (a) rGO by SEM and (b) GO by TEM.

Preparation of graphene-based nanofluids with long term stability is a great challenge. Graphene is highly hydrophobic and the strong van der Waals interactions between nanoparticles are difficult to balance. Among the reported strategies for graphene-based nanofluid preparation, using GO is a quite simple method since oxygen-containing groups are introduced at the platelets surface during the GO preparation by the Hummers method which is highly oxidative. These functional groups are able to improve affinity of graphene with water and to induce repulsive interactions between the nanosheets. However, the long term stability is difficult to achieve. Since GO is in the form of nanosheets of more than 2 layers, the prepared nanofluids are dark even at quite low concentration (> 0.02 vol.% of GO). And it can be difficult to be sensitive to a slow starting destabilization of the nanofluid. Long-term stability is one of the most important parameters to envisage graphene-based nanofluids for thermal applications. Moreover, in thermal energy conversion or storage systems, the working fluid undergoes modifications of the physical surrounding parameters: temperature but also motion and shearing in circulating fluid systems or even phase change in thermal energy storage devices.

Fig. 2 shows thermal conductivity evolution as a function of time for a nanofluid of GO at low concentration (0.01 vol.%) and at 20 °C. At the beginning of the experiments the GO solution appears quite homogeneous without any visible aggregates and its thermal conductivity is high above that of water. Its stability turns out to be quite poor since the first minutes the measured thermal conductivity slowly decreases. Even in these light color solutions, aggregates are not visible and only after several hours, agglomeration and sedimentation are detectable with eves. A sediment is visible in the nanofluid after being settled for 8 hours. The poor stability of GO, even if it is often denied, is not surprising and can be simply explained by formation of H bonding between alcohol and ether groups present at the GO surface and water molecules [7,9].



Figure 2 Thermal conductivity of a GO solution at a concentration of 0.01 vol.% of GO in water as a function of time at 20 °C. Visual aspects of the GO solution at the beginning of the measurements and after 8h (without shaking).

Graphitic structure of GO is usually highly damaged by the presence of a high level of functional groups and defects at its surface. Reduction of GO allows to partially restore the sp² bonding structure which has the great advantage to guarantee better properties including thermal conductivity. In this work, the two most common reductive agents, N₂H₄ and NaBH₄, were used. Their effect regarding the induced visual stability of the rGO nanofluids is compared depending on the used concentration conditions (Fig. 3). As usually reported, after reduction, the solutions appear darker than the corresponding GO nanofluids meaning that the reduction reaction has occurred. At low GO/rGO concentration (0.01 vol.%), the nanofluids appear very stable at low and high reductive agent concentration for both N₂H₄ and NaBH₄ (Figs. 3a, 3b, 3f and 3g). 1 month after their preparation, no aggregates and no sedimentation are

noticeable. At higher rGO concentration (0.1 vol.%), reduction with NaBH₄ is not detrimental to the stability (Figs. 3i and 3j) whereas by using N_2H_4 at high concentration (0.05 vol.%, Fig. 3d), precipitation of rGO in the form of gel occurs. After freeze-drying (Fig. 3e), graphene nanosheets appear interconnected in the obtained aerogel. High reduction level is probably responsible for attractive forces between the rGO platelets inducing a self-assembling phenomenon. This latter is slowed as the N₂H₄ concentration is low, the attractive interactions being certainly less strong since the reduction level is reduced; aggregates are however visible in the nanofluid (Fig. 3c). For low rGO concentration even at high N₂H₄ concentration, no destabilization can be noticed but very long term stability might be compromised.



Figure 3 Visual aspect of the rGO nanofluids 1 month after their preparation with different concentration conditions: a) and b) 0.01 vol.% GO with 0.005 vol.% and 0.05 vol.% N₂H₄, respectively; c) and d) 0.1 vol.% GO with 0.005 vol.% and 0.05 vol.% N₂H₄, respectively; f) and g) 0.01 vol.% GO with 0.01 wt.% and 0.1 wt.% NaBH₄, respectively; i) and j) 0.1 vol.% GO with 0.01 wt.% and 0.1 wt.% NaBH₄, respectively; i) and j) 0.1 vol.% GO with 0.01 wt.% and 0.1 wt.% NaBH₄, respectively; i) and j) 0.1 vol.% GO with 0.01 wt.% and 0.1 wt.% NaBH₄, respectively; i) and j) 0.1 vol.% GO with 0.01 wt.% and 0.1 wt.% NaBH₄, respectively; i) and j) 0.1 vol.% GO with 0.01 wt.% and 0.1 wt.% NaBH₄, respectively; i) and j) 0.1 vol.% GO with 0.01 wt.% and 0.1 wt.% NaBH₄, respectively; i) and j) 0.1 vol.% GO with 0.01 wt.% and 0.1 wt.% NaBH₄, respectively; i) and j) 0.1 vol.% GO with 0.01 wt.% and 0.1 wt.% NaBH₄, respectively; i) and j) 0.1 vol.% GO with 0.01 wt.% and 0.1 wt.% NaBH₄, respectively; i) and j) 0.1 vol.% GO with 0.01 wt.% and 0.1 wt.% NaBH₄, respectively; i) and j) 0.1 vol.% GO with 0.01 wt.% and 0.1 wt.% NaBH₄, respectively; i) and j) 0.1 vol.% GO with 0.01 wt.% and 0.1 wt.% NaBH₄, respectively; i) and j) 0.1 vol.% GO with 0.01 wt.% and 0.1 wt.% NaBH₄, respectively; i) and j) 0.1 vol.% GO with 0.01 wt.% and 0.1 wt.% NaBH₄, respectively; i) and j) 0.1 vol.% GO with 0.01 wt.% and 0.1 wt.% NaBH₄, respectively; i) and j) 0.1 vol.% GO with 0.01 wt.% and 0.1 wt.% NaBH₄, respectively; i) and j) 0.1 vol.% GO with 0.01 wt.% and 0.1 wt.% NaBH₄, respectively; i) and j) 0.1 vol.% GO with 0.01 wt.% and 0.1 wt.% NaBH₄, respectively; ii) and j) 0.1 vol.% GO with 0.01 wt.% and 0.1 wt.% NaBH₄, respectively; ii) and j) 0.1 vol.% GO with 0.01 wt.% and 0.1 wt.% NaBH₄, respectively; ii) and j) 0.1 vol.% GO with 0.01 wt.% and 0.1 wt.% NaBH₄, respectively; ii) and j) 0.01 wt.% and 0.1 wt.% NaBH₄, respectively; ii) and ji) 0.1 vol.% GO wterpectively; ii) and ji) 0.1 vol.% GO wterpectively;

These results show that stability of GO/rGO is sensitive to the graphene materials concentration and that for long term stability of rGO, NaBH₄ has to be preferred as reductive agent. Moreover, N₂H₄ is reported to be able to introduce C-N groups that behave as impurities since they have significant effect on the electronic structure of the resulting graphene; and such heteroatoms are difficult to be removed in a simple way. On the contrary, NaBH₄ does not lead to any additional heteroatoms to the graphene structure. NaBH₄ is most effective at reducing C=O species leading to additional alcohols at the rGO surface. The reduction in hydrophilicity using NaBH₄ consequently occurs at a lesser degree than N₂H₄, which is certainly the reason for the stability observed for rGO nanofluids prepared with NaBH₄. Thermal measurements of these rGO nanofluids are under progress.

IV. CONCLUSION

Stability of GO and rGO nanofluids are analyzed and discussed regarding the possible chemical interactions between the nanomaterials. GO nanofluids prepared by the Hummers' method have shown low stability, but after reduction, stability of rGO nanofluids was strongly improved. rGO nanofluids behave differently depending on the used conditions (nature of the reduction agent, starting GO concentration, reductant content). With N₂H₄, decrease in hydrophilicity is too strong leading to nanofluid destabilization. NaBH₄ is, on the contrary, a better reduction agent since long term stability could be achieved in the whole condition range investigated.

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