

# ULTRADISPERSED NANOCOMPOSITES MEMBRANE OF COPPER@REDUCED GRAPHENE OXIDE/PVDF FOR ENHANCED THERMAL CONDUCTIVITY

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## ABSTRACT

Poly (vinylidene fluoride) (PVDF) is semi-crystalline thermoplastic polymer with excellent thermal stability, film-forming property and much more advantages over metal materials such as low density, corrosion resistance, integrated processing and low cost. So as to enhance its thermal conductivity, the nanoarchitecture of copper@reduced graphene oxide (RGO) was designed to improve it. The well-dispersion of graphene in PVDF and the synthesis of copper@RGO with different copper content were studied to improve the thermal conductivity of the nanocomposites. The nano copper was considered as the effective heat transfer medium to reduce the interface thermal resistance between graphene and PVDF chain segment. The graphene oxide (GO) was fabricated by modified Hummers method and the graphene was surface modified before used. Copper@RGO was fabricated by microwave liquid phase method. Then the copper@RGO were doped with PVDF to prepare membrane. The morphology, structure and thermal conductivity of the composite membranes with different additive content were characterized and analyzed. The thermal conductivity of composite membranes were significantly improved with the addition of graphene. This tendency was further enhanced by the application of copper.

## 1 INTRODUCTION

Currently, most of heat transfer apparatus is prepared with metal materials, for the good heat resistance, excellent mechanical properties and high heat transfer efficiency. However, there are still many deficiencies, such as high cost, scaling surface and poor corrosion resistance (leading to reduced heat transfer performance and rising energy consumption, as well as environmental pollution from chemical descaling). For these deficiencies, researchers in science, technology and engineering fields have been making their efforts on seeking for alternative polymer materials with high thermal conductivity<sup>[1-3]</sup>. As we all know, most polymeric materials enjoy superior advantages such as corrosion resistance, low density, fouling resistance, facile processing and low cost. The defects of metal materials in heat transfer apparatus can be supplemented by polymers, with great potential in the application of heat exchanger.

PVDF is an excellent thermoplastic polymer, with good chemical stability, heat resistance and stain resistance. In recent years, PVDF has been widely applied in many fields such as chemistry engineering, electronics and food industry with outstanding mechanical properties, wide processing temperature range and easiness in the fabrication of films<sup>[4]</sup>. PVDF can be dissolved in various solvents including N-methylpyrrolidone (NMP), N,N-dimethylformamide (DMF), dimethylacetamide (DMAC) and dimethylsulfoxide (DMSO). However, the application of PVDF in the field of heat exchanger is limited for its poor thermal conductivity. Therefore, increased heat transfer performance of PVDF will enable more applications in fields of heat transfer.

For improving the thermal conductivity of polymers, various thermal conductive fillers were added to the matrix for preparing thermal conductive composites<sup>[5-7]</sup>. The PVDF composites were prepared via nano-carbon fillers including zero-dimensional superfullerene (SF), one-dimensional carbon nanotube (CNT) and two-dimensional graphene sheets (GS) by compression molding method. The thermal conductivity of PVDF composites with 20 wt% two-dimensional GS reaches a maximum 2.06 W/(m K)<sup>[5]</sup>. Xu has investigated the thermal conductivity of epoxy and PVDF composites filled with AlN powder and whisker. When the particles and whiskers of AlN were mixed in a volume ratio of

25.7:1, and the total volume of AlN reached 60%, the highest thermal conductivity of 11.5 W/(m K) was attained. When the total volume of AlN was relatively low at 25%, with the particles and whiskers of AlN in a 1:1 volume ratio, the thermal conductivity of PVDF-matrix composite was 1.73W/(m K). However, with the addition of AlN, the tensile strength, modulus and toughness of the composites would be attenuated<sup>[8]</sup>. Graphite nanoplatelets (GNPs) were added to the epoxy for preparing thermal interface material. When the volume fraction of GNPs was approximately 25%, the thermal conductivity of composite was increased by 6.44 W/(m K)<sup>[9]</sup>. Comparing with PVDF matrix composite, epoxy resin matrix composite needs curing agent to be added and the curing cycle is shorter and there may be not enough time for the fillers to agglomerate. This may be one reason why the thermal conductivity of epoxy resin matrix composites is more outstanding. However, the thermal and electrochemical stability, mechanical properties and toughness of PVDF is much better than that of epoxy resin. For our research, we chose PVDF as the composite matrix and the thermal conductivity of the composite materials was studied under the low weight loading of fillers.

At present, graphene, as the representative of the new carbonaceous material, has attracted wide attentions. Graphene is a single layer of carbon atoms arranged as two-dimensional honeycomb crystal. In 2004, Andre Geim and Konstantin Novoselov in the University of Manchester successfully prepared the stable graphene for the first time<sup>[10]</sup>. Since then, graphene has become a research hotspot in the field of materials. There are many excellent properties in graphene, such as high electron mobility at room temperature<sup>[11]</sup>, high thermal conductivity<sup>[12]</sup> and good mechanical properties<sup>[13]</sup>. Thus, it has broad application prospects in the fields of electronic device, biological and chemical sensors, energy storage devices and composite materials<sup>[14-16]</sup>. The two-dimensional plane structure of graphene enables very high thermal conductivity, thus, it has become one of the most ideal materials for improving thermal conductivity of polymers.

So far, researchers have developed several preparation methods for graphene, including mechanical exfoliation, chemical vapor deposition and oxidation-reduction method<sup>[17]</sup>. The oxidation-reduction method is the most common method for graphene preparation because of its low cost, high yield and batch production. Many reductants can be applied for reducing graphene oxide and the most common reductants are hydrazine hydrate<sup>[18]</sup> and sodium borohydride<sup>[19]</sup>. Hydrazine hydrate is high in reducibility and dose not react with water. Thus, it is one of the most desirable reductants for reducing graphene oxide<sup>[20]</sup>. For the reduction of aqueous solution of graphene oxide, the efficiency of sodium borohydride is higher than hydrazine hydrate, while it can slowly react with water. Other reductants such as hydroquinone<sup>[21]</sup> and strong alkaline solution<sup>[22]</sup> may also be applied for reducing graphene oxide.

In this study, graphene was added to PVDF matrix for improving the thermal conductive performance of composite membranes. First, GO was synthesized with modified Hummers method and dispersed to be graphene oxide. Then the copper@RGO was fabricated by microwave liquid phase synthesis method. Third, the copper@RGO /PVDF composite membranes were prepared with solvent casting method. Their morphology, structure and thermal conductivity were investigated with different contents of graphene in the composite membranes.

## 2 EXPERIMENTS

### 2.1. Materials

The natural flake graphite (powder) (national medicine group chemical reagent co., Ltd, particle size is 20 um, purity 99%. Potassium permanganate (mass fraction of 98%) , Concentrated sulfuric acid (mass fraction of 98%) and Hydrogen peroxide(mass fraction of 30%) were purchased from Beijing chemical reagent factory, Copper sulfate(YuanLi Chemical, Tianjin, China) and Arabic gum (Guan fu Fine Chemical Research Institute, Tianjin, China) were grade AR. Hydrazine hydrate (98 wt%), N-methylpyrrolidone (NMP, 98% purity) were purchased from Aladdin (Shanghai, China). PVDF 904 was supplied by Yuanye Chemical Technology Co., Ltd. (Shanghai, China), with the density of 1.75–1.77 g/mL, melt flow index of 0.5–2.0 g/10 min and melt point of 156–165 °C.

### 2.2. Preparation of graphene

graphite oxide was prepared by previously modified Hummers method<sup>[23]</sup>. 1.5g graphite and 1.5 g KNO<sub>3</sub> were added to the 69 ml concentrated sulfuric acid, the mixture under water bath heating and electromagnetic stirring, when the temperature get to 40 °C, 9.0g KMnO<sub>4</sub> was slowly added to hybrid

species, and then maintain the reaction at 40 °C for 6 h, six hours later, 120 ml deionized water were slowly added in the reactor and the temperature was adjusted to 60 °C. After 30 min, 300 ml deionized water were added in it and continue to 4 ~ 5 min. To reduce the rest of  $\text{KMnO}_4$  and  $\text{MnO}_2$ , 30%  $\text{H}_2\text{O}_2$  was added in the reactor, until the reaction liquid change to bright yellow.

A certain amount of GO was dispersed in an aqueous solution, to give a tan suspension. Then, the solution was dispersed with ultrasonic cleaner for 2 h. A stable dispersion solution of graphene oxide could be obtained. The obtained product was filtered and washed with ethanol and deionized water for several times. The product was thoroughly dried at 60 °C in vacuum oven and the graphene powder was saved at room temperature for further use.

### 2.3. Preparation of surface-modified graphene oxide

The prepared GO powder was dispersed in 10 ml distilled water. Alanine and NaOH solution (40 ml) were added. The obtained solution mixture was stirred for 48 h at 60 °C. At the end of the reaction, the dispersed solution was treated with ethanol. And the mixture was washed by  $\text{H}_2\text{O}$ . Finally, the product was dried at 60 °C.

### 2.4. Preparation of nano copper@RGO

The microwave reaction device was used to this part. A certain amount of GO was dispersed in an aqueous solution with the concentration of 1.5mg/ml. Five components samples were prepared at the same conditions. 0.052,0.104,0.208,0.3125,0.55g  $\text{CuSO}_4$  were added in 10 ml water and the solutions was magnetic stirring for 15 min. Then the GA solution was added to the  $\text{CuSO}_4$  solution and keep stirring for 60 min. The GO solution was put in the ultrasonic cleaner for 2h. After 2 hours, the  $\text{CuSO}_4$ /GA solution was poured to the GO solution. The mixture was magnetic stirred for 30 min and under ultrasonic dispersion for another 2h. Finally, the solution was put in the microwave reaction device with the condition of 600W, 80 °C, 2min. The product was washed by ethanol for two times and then dried at 60 °C for a night in the vacuum oven.

### 2.5. Preparation of the nanocomposite membrane

2g PVDF was dispersed in the NMP. An appropriate amount graphene was dispersed in additional NMP by magnetic stirred for 10 min followed by sonicated for 2 h to obtain the dispersion. The dispersion of graphene was added to the PVDF in NMP and stirred for 12 h at 40 °C to form a homogeneous solution, Then the solution was poured into a mold under 80 °C for 8 h. Then heating to 120 °C for 12 h to get the membrane for the development characterization.

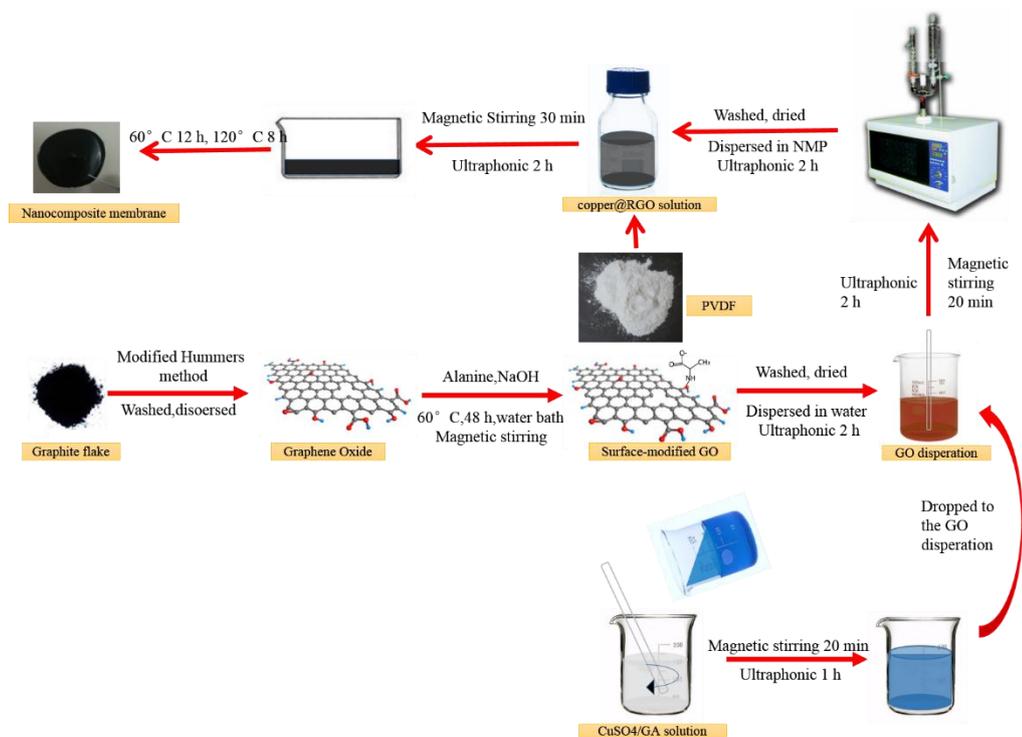


Figure 1: Schematic illustration of the fabrication of the nanocomposite membrane

## 2.6. Characterization of membrane

The morphologies of graphene, copper@RGO and composite membranes were observed with scanning electron microscopy (SEM, S-4800, Hitachi, Japan). The composite samples were imaged by first fracturing in liquid nitrogen, then fixed on the conductive adhesive and sputtered with a thin layer of gold.

The graphene was observed with atomic force microscopy (AFM, VEECO Dimension 3100, Bruker, Germany) on silicon substrate. The sample for AFM was prepared as follows: graphene powder was dispersed in NMP solution and the suspension was dropped on the silicon substrate. The AFM was under ambient conditions and scanned in tapping mode.

The GO and graphene were observed with the Fourier transform infrared spectroscopy (FTIR, TENSOR 27, Bruker, Germany) with KBr powder as the background. The wavenumber was ranged from 4000 to 400  $\text{cm}^{-1}$ .

The alignment of graphene in the composite membranes was determined with X-ray diffraction (XRD) (D8-Focus, AXS Ltd., Germany) and polarized Raman spectroscopy (DXR Microscope, America).

The tensile strength test of composite membranes was performed in a small universal testing machine. The membrane samples were cut into strips with a width of 10mm. The initial length between the two loading ends was 100 mm. The thickness variation of the membrane sample was less than 10%. The samples were slowly stretched with a constant speed of 10  $\text{mm min}^{-1}$  until failure and the tensile strength was recorded.

The thermal conductivity of composite membranes was measured with a thermal conductivity meter (TPS, China). The thickness of membrane for testing was 300  $\mu\text{m}$ . The data was collected for 3 s with a time interval of 3 min, which was the average of 4 repeats. The applied voltage was 1.5 V.

## 3. RESULTS AND DISCUSSION

### 3.1. Characterization of GO and surface-modified GO

Graphene before and after surface modification was prepared and the morphology was characterized with SEM image on the micron scale structure of graphene. Because of few layers, the

graphene layers show the wrinkled topography (Fig. 1a). With SEM image, the surface-modified graphene shows the more wrinkled morphology of thin sheet (Fig. 1b).

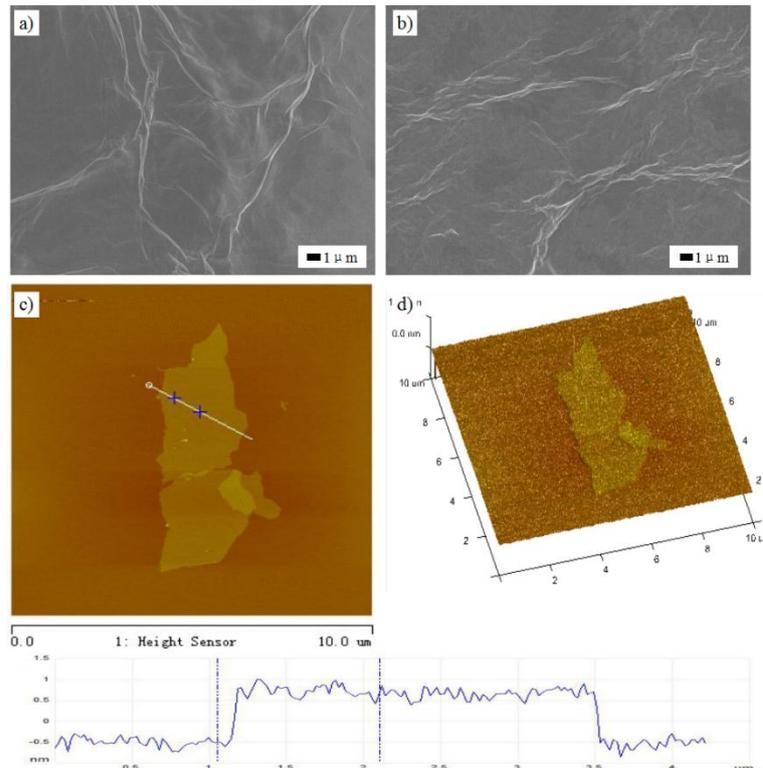


Figure 2: The characterization of GO. a) SEM image of GO. b) SEM image of surface-modified GO. c) - d) AFM images of GO and the thickness of graphene

The thickness of graphene layers was characterized to be 0.8 nm–1.0 nm with AFM (Fig. 1c-d). It suggests that the single layer graphene was successfully prepared [24]. In general, the thickness of single layer graphene is about or less than 1 nm. The XRD image indicates that the graphite was oxidized totally. There is a characteristic peak on  $11.8^\circ$  means graphene oxide.

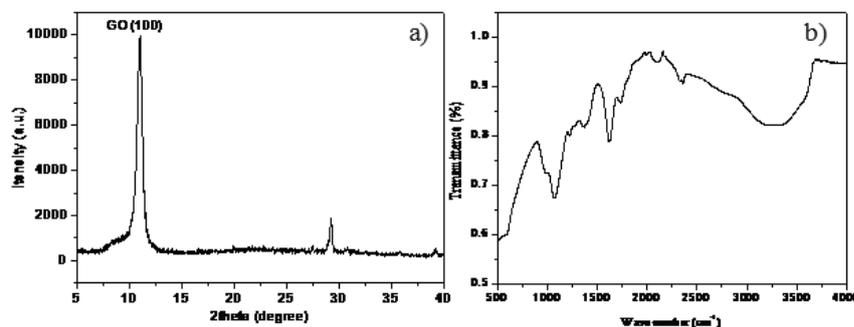


Figure 3: The characterization of GO. a) XRD image of GO. b) The FTIR spectrum of GO

The IR spectrum of GO is provided (Fig. 3b). A broad, strong absorption peak in the vicinity of  $3430\text{ cm}^{-1}$ , which is attributed to the stretching vibration peak of  $\text{OH}$ . The absorption peak at  $1725\text{ cm}^{-1}$  is the stretching vibration peak of  $\text{C=O}$  in the carboxyl group of GO. The absorption peak at  $1630\text{ cm}^{-1}$  may be the bending vibration peak of the  $\text{C=O}$  and the peak at  $1110\text{ cm}^{-1}$  is the vibration peak of  $\text{C-O-C}$ . With the result of IR spectrum, the functional group of  $\text{OH}$ ,  $\text{COOH}$ ,  $\text{C=O}$ ,  $\text{C-O-C}$  can be observed. It confirms that the graphite was successfully oxidized to GO.

### 3.2. Characterization of copper@RGO

The copper@RGO with different copper content were studied (Fig. 4-5). The XRD patterns of RGO with different copper content are shown to demonstration the influence of composite copper content on the RGO. When the copper content is less than 10 ct%, the crystal structure and crystallinity of RGO are identical to that of the higher content. When the copper content increasing, the reduction condition was increase. Gradually, the GO character peak was decreased.

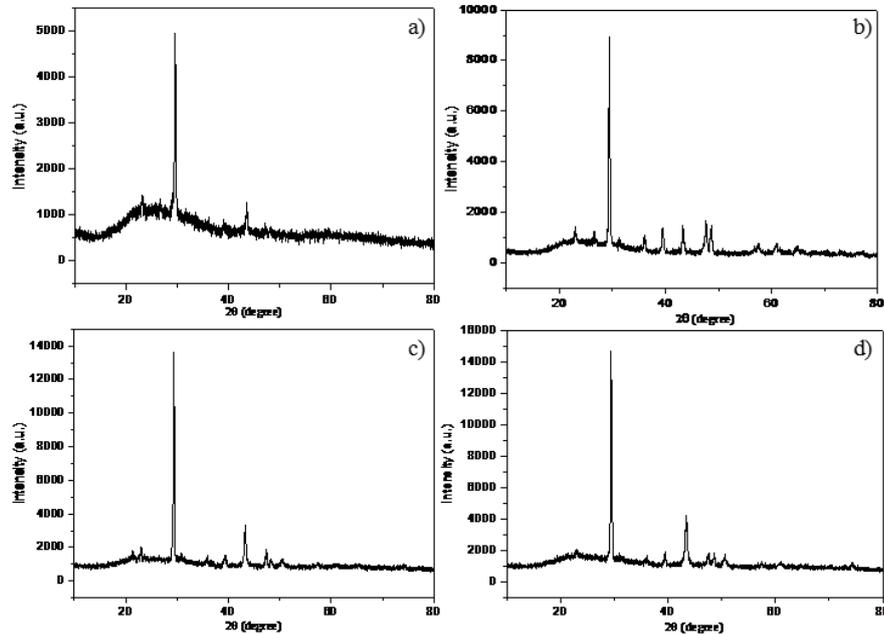


Figure 4: XRD patterns of RGO with copper content of 5ct%, 10ct%, 20ct% and 30ct%

When the content of copper is increasing(Fig. 5), the morphology of RGO was characterize with SEM. It can be observed that the size of the copper nano nods change to small and the number was increased. It is observed from the diagram that the nano copper spheres are attached to the expanded graphene sheet.

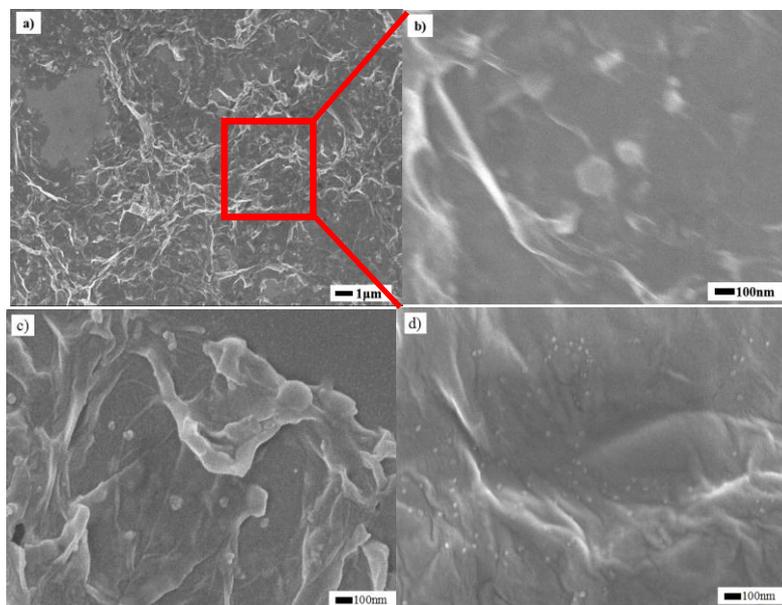


Figure 5: SEM images of RGO with copper content of 5ct%, 10ct% and 30ct%

When the copper content lower than 1 ct %, the copper particles have a bigger scale, they attached to the graphene layers on the number of less and uneven distributed. With increased levels of nanocopper, copper nano particles size reduced by 50 nanometers to a few nanometers, distribution is more homogeneous, graphene layers of size is not damaged.

### 3.3. Characterization of copper@RGO/PVDF nanocomposite membrane

The XRD patterns of pure PVDF membrane and copper@RGO/PVDF composite membranes with different copper content are shown to demonstration the crystallinity of composite membranes and spatial orientation of graphene (Fig.7). When the copper content is 0 ct%, the crystal structure and crystallinity of copper@RGO/PVDF composite membranes are identical to that of pure PVDF membrane. When the copper content is 5 ct%, a weak diffraction peak can be observed at  $2\theta = 26^\circ$ , which corresponds to the diffraction peak of graphite (002) plane.

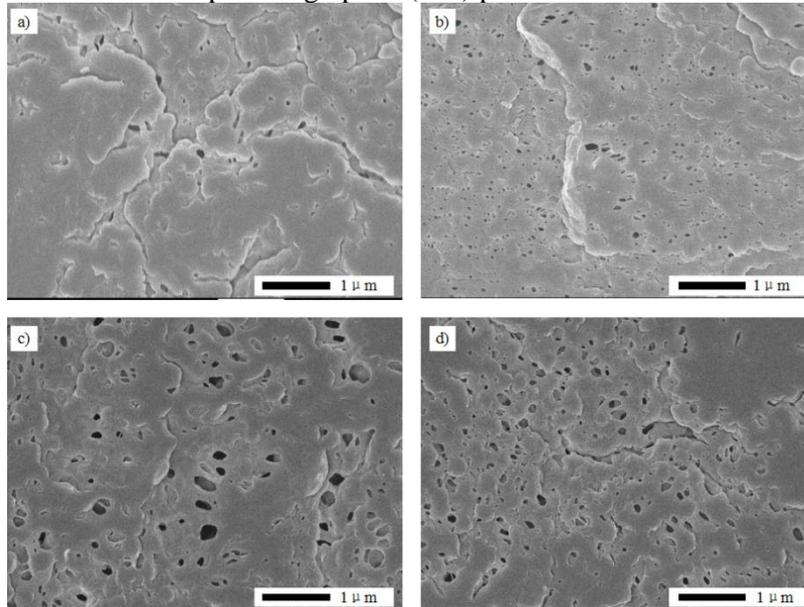


Figure 6: SEM images of copper@RGO/PVDF membrane with different copper content of 5ct%, 10ct%, 20ct%, 30ct%

The SEM images of the nanocomposites was studied to explore the surface topography. For the pure PVDF membrane, it can be find that more and more void appeared with the increase of content.As the copper content increases, the surface appearance of nanocomposites is not particularly noticeable. In addition to the number of holes in the surface, the level of flatness has not changed.

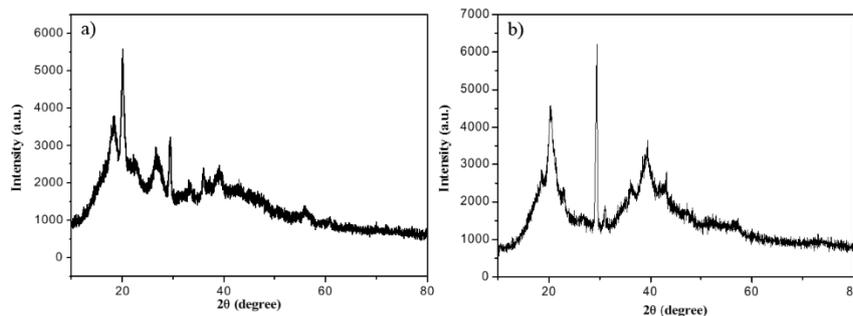


Figure 7: XRD patterns of PVDF membrane with 10ct%copper@RGO content of 0wt% and 5wt%

### 3.4. Thermal conductivity of copper@RGO/PVDF nanocomposite membrane

The thermal conductivity of PVDF composite membranes with different copper content is shown (Fig. 8).With the increase of copper content, the thermal conductivity of graphene/PVDF composite membranes is firstly increased and then decreased.

When the copper content is less than 20 wt%, graphene can be uniformly dispersed in the composite membranes that promotes the thermal conductivity of the membranes. However, due to the low content, the graphene sheets are separated by poor thermal conductive PVDF molecules.

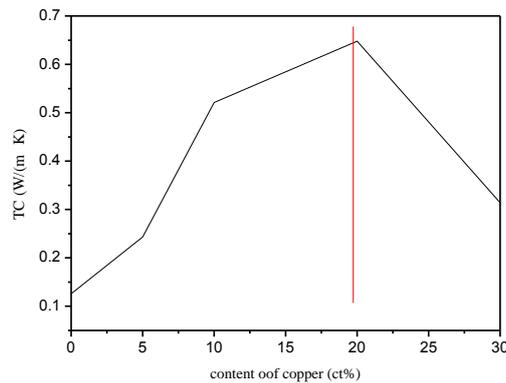


Figure 8: Thermal conductivity of copper@RGO/PVDF nanocomposite membrane with different copper content of 5ct%, 10ct%, 20ct%, 30ct%

The maximum value of 0.614 W/(m K) is obtained when the content of copper reaches to 20 ct%. It is increased by 425% compared to the pure PVDF membrane. The enhancement of thermal conductivity is generally increased by doping thermal conductive fillers, which is also the most facile way to greatly increase the thermal conductivity of PVDF. When the content of copper is above 20 ct%, non-significant improvement can be observed in the thermal conductivity of composite membranes. It maintains within a relatively stable range.

#### 4. CONCLUSIONS

In this study, the graphite oxide was prepared from the natural flake graphite based on the Hummers method, and then the graphene was loaded with nanocopper. The copper@RGO/PVDF composite membranes with various contents of copper were prepared by the solvent casting method. Graphene was successfully prepared and well dispersed in PVDF matrix. After the location with copper, the arrangement of graphene was more in ordered in the matrix, which was perpendicular to the membrane surface and consistent with the current direction. Both the crystallinity and thermal stability of composite membrane were improved after alignment. When the content of copper was 20 ct%, the thermal conductivity of the composite membrane was increased by 325% than that of pure PVDF.

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