

# Improved Performance of Thin Film Nanocomposite (TFN) Nanofiltration Membrane-by the Addition of Functionalized Graphene Oxide for Desalination Application

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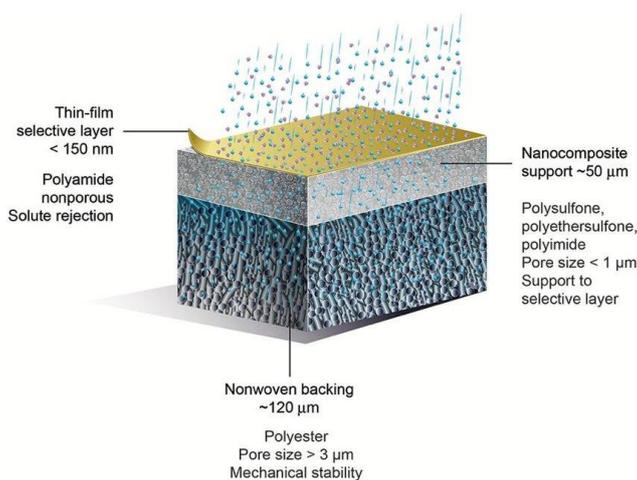
**Abstract:** To develop a high-performance thin-film nanocomposite (TFN) nanofiltration (NF) membrane, the functionalized graphene-based nanomaterial was synthesized by combining graphene oxide (GO). Hyperbranched polymer, which has been used as a novel nanofiller and successfully integrated into the active polysulfone (PSf) layers through an interfacial polymerization (IP) process. Fourier Transform Infrared Spectroscopy (FTIR) and Field-emission Scanning Electron Microscope (FESEM) were used to characterize the NF membrane obtained and its performance was evaluated according to the water flux with the addition of *f*-GO. TFN0.05 membrane exhibit the optimal, and salt rejection rate. The influence of *f*-GO on the morphologies, properties, and performance of TFN NF membranes was investigated. The addition of the *f*-GO membrane exhibited the optimal water flux without the sacrifice of the salt rejection. It was found that the introduction of functionalized graphene-based nanomaterial nanosheets favored the formation of a thinner and smoother nanocomposite active layer with enhanced hydrophilicity. As a result, TFN NF membranes demonstrated a superior permease activity over the conventional thin-film composite (TFC) membranes.

**Keywords:** Thin-Film Nanocomposite, Thin-Film Composite, Nanofiltration, Graphene Oxide, Polysulfone.

## 1. Introduction

With a continuing decline of available freshwater supplies and an increasing demand for fresh water due to population booming and worldwide industrialization, membrane technologies have gained great attention in recent years. Nanofiltration (NF) membrane has been extensively studied in recent years due to its advantages of producing promising water flux a relatively low operating pressure while exhibiting an excellent separation rate against divalent salts [1]. Nanofiltration is a process of

intermediate reverse osmosis and ultrafiltration, which enables higher flux and lower operating pressure than reverse osmosis, and could afford a high rejection of organic molecules with a molecular weight cutoff (MWCO) ranging from 100 to 1000 Da or multivalent ions. [2]. High energy efficiency coupled with excellent divalent salt rejection has made the NF membrane a good candidate for a pre-treatment in the desalination. Unlike the asymmetric NF membrane prepared by the phase inversion method, the thin film composite (TFC) NF membrane prepared by the IP technology shows higher water permeability without affecting the excellent selectivity [3] [4]. Among various nanofiltration membrane fabrication technologies, interfacial polymerization (IP) has been developed as the main method for preparing polyamide TFC nanofiltration membranes. The construction of the TFC membrane is shown in Figure 1.



**Figure 1: Architecture of thin-film composite membrane (TFC)**

A thin-film nanocomposite (TFN) membrane is a new type of composite membrane prepared by the (IP) process with the addition of nanoparticles. Due to the unique functions of inorganic nanofillers, the resulting TFN membranes show great potential in overcoming the flux suppression trade-off of TFC membranes. These include improved surface hydrophilicity, increased surface roughness, excellent anti-fouling, and anti-bacterial properties [5]. The interfacial polymerization process is self-inhibiting through a limited supply of reactants to the already formed layer, resulting in an extremely dense thin film of thickness ranging from 50 nm to several hundred nanometers [6]. The thin film that formed at the top of the porous support will determine the overall solute retention and permeate flux, which can be optimized by varying the type and concentration of the monomer in each solution, the monomer ratio, and the reaction time of the interfacial polymerization process. Considerable attempts have been made to improve the comprehensive performance of the TFN nanofiltration membrane.

Hence, this study aims to improve the performance of TFC by adding the nanoparticles, namely, functionalized Graphene Oxide (*f-GO*). The *f-GO* will be added to the polyamide layer during the preparation of the interfacial polymerization process. The morphology of both pristine TFC and prepared TFN membranes will be investigated using Fourier Transform Infrared Spectroscopy (FTIR), Atomic Force Microscopy (AFM), and Field-emission Scanning Electron Microscope (FESEM). Thus, the separation performance of both fabricated membranes will be further analyzed.

## 2. Materials and Methods

### 2.1 Materials

Both Piperazine (PIP) and Trimethyl chloride (TMC) monomers was purchased from Sigma Aldrich. The monomers were to establish the polyamide (PA) selective layer. n-Hexane as the organic solvent was obtained from Merck. Graphite powder (<20  $\mu\text{m}$ ) (obtained from Sigma Aldrich) was used

to functionalize graphene oxide (GO) which is used for modification. Charged solutes were used to test the NF performance of the resulting membrane during water suppression using inorganic salts, including sodium sulfate ( $\text{Na}_2\text{SO}_4$ ) and magnesium sulfate ( $\text{MgSO}_4$ ). Both salts were obtained from Merck. The laboratory provided all other chemical reagents. During the test, deionized water was used.

## 2.2 Graphene Oxide (GO)

Graphene Oxide (GO) is one of the suitable nanoparticles to enhance the hydrophilicity of the membrane. GO is usually prepared by Hummer's method. GO contains functional groups to make it more dispersed in the polymeric solution. By incorporating GO into the membranes, improved properties for water purification technologies can be achieved. The GO-incorporated membranes have improved fouling resistance by reducing surface roughness and increasing hydrophilicity. GO has an abundance of oxygenated functional groups, providing possible use in various applications, after chemical modification.

## 2.3 Preparation of TFN membrane

TFN NF membrane was prepared via an in-situ interfacial polymerization process between PIP and TMC. Polysulfone (*PSf*) substrate was initially taped onto the glass plate followed by 2 minutes of immersion in an aqueous solution of 2.00 % (w/v) PIP [7]. The excess solution from the impregnated membrane surface was eliminated using a soft rubber roller [8]. The membrane was immediately immersed into the n-hexane solution of 0.20 % (w/v) TFC containing 0.05 wt.% of *f-GO* nanoparticles for 60 s, which resulted in the in-situ formation of an ultra-thin polyamide (PA) layer over the microporous *PSf* substrate. Subsequently, the resulting membrane was cured at 60 °C for 5 min and finally was thoroughly washed with de-ionized water before storage in de-ionized water at 5 °C before use. The prepared TFN NF membrane was denoted as TFN0.05. Besides, the TFC membrane was prepared using the same method without the addition of *f-GO* nanoparticles and denoted as TFC membrane throughout the paper. Table 1 shows the recipe for the preparation of composite membranes.

**Table 1: Preparation of composite membranes**

Membrane	<i>f-GO</i> (wt.%)	Monomer con. PIP (wt/v%)	Monomer con. TMC (wt/v%)
TFC	0	2.0	0.15
TFN0.05	0.05	2.0	0.15

## 2.4 Preparation of Cross – Flow Filtration

The technique that will be used in this experiment is cross-flow filtration (CFF also known as tangential flow filtration, TFF). According to this technology, the pressure difference between the filter drive components that are smaller than the pores through the filter [9]. As the feedwater passes tangentially along the surface of the water, components from the feed water that are larger than the filter pores are retained where it passes along the membrane to be restored to the feed water reservoir. A solution that is directed to the surface of the membrane is called the feed. The solution that passes through the membrane surface and returns to the feed reservoir is the retentate. This solution is usually pumped back to the feed reservoir and recirculated. The solution that passes through the membrane is permeated. In the cross-flow filtration, the fluid feed stream runs tangential to the membrane surface and leading to a pressure differential across the membrane [10]The feed flow through the membrane tube at an elevated pressure across the membrane, where the high flow causes turbulence to occur. The process is called cross flow due to the 90 ° angle between the feed flow and the membrane. The techniques have been improved over the years as can be observed [11] using a hydrophilic membrane. The presence of a hydrophilic medium ensures that clean water can permeate through the membrane while the oils can be repelled where they will end up in the backwash. The advantage of cross-flow filtration lies in the direction of the feed where there is a continuous flow of fluid that washes away the

flux that blocks the pores of the membranes. This eliminates the need for frequent and labor-intensive maintenance. Flow in the various process lines may also be regulated by valves with flow restrictors. Together, the controlled pump rates and valve restriction create pressure across the membrane that drives the filtration process.

## 2.5 Membrane Performance Test

The conductivity meter consists of a probe to measure conductivity. A small electric current flow between two electrodes and is separated by a certain distance. If the concentration of ions in the solution is high, its conductivity is high, and it will produce a fast current [12]. The conductivity meter to be used in this experiment is made by the company Mettler Toledo. This is a professional company from the United Kingdom that produces laboratories and industrial equipment. In this experiment, a conductivity meter was used to determine the electrical conductivity measured in the solution due to the salt concentration. Other impurities can also trigger the electrical reading of the conductivity meter. Therefore, the test must be performed in a controlled environment where no impurities will affect the results obtained from the conductivity meter.

### 2.5.1 Permeate Flux

Permeate flux describes the quantity of permeate produced during membrane separation per unit of time and membrane area. The flux is measured in liters per square meter per hour Liter/m<sup>2</sup>/Hours (LMH). The flux of solvent through the membrane is expressed as [13]:

$$F = \frac{V}{t A} \quad Eq. 1$$

Where F is the flux of the solvent, V is the permeate flow in liter/hour, A is the surface area of the membrane system in m<sup>2</sup> and t is the experimental time, respectively.

### 2.5.2 Salts rejections

A custom-built cross-flow NF system with an active filtration area was used to characterize the membrane performance. The permeability of the membrane is usually related to the concentration of solutes that are allowed to pass through the filters. By calculating the fraction of the permeate concentration and multiplied by 100%, the efficiency or rejection of the membranes can be obtained. Salt Rejection (R) was calculated using the following equation [13];

$$R = \left(1 - \frac{C_p}{C_f}\right) \times 100\% \quad Eq. 2$$

Where CP and CF are the conductivity values of permeate and feed solutions, respectively.

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## 2.6 Membrane of Characterization

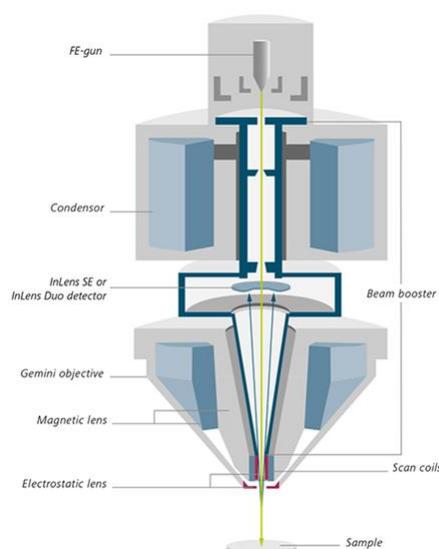
### 2.6.1 Fourier Transform Infrared Spectroscopy (FTIR)

This is an analytical technique used to identify organic, polymeric, and in some cases, inorganic materials. The FTIR analysis method uses infrared light to scan test samples and to observe chemical

properties. FTIR was used to study the molecular interactions between nanocrystals and polyamide, and between polyamide and polyimide, and to observe the chemical changes that occur after the posttreatment. A Bruker Vertex 70 Spectrophotometer with a DTGS detector and diamond ATR Golden Gate was used [14].

### 2.6.2 Field-emission Scanning Electron Microscope (FESEM)

The Field-emission Scanning Electron Microscope (FESEM) is an instrument like the SEM that can provide a wide variety of information from the sample surface but with higher resolution and a much greater energy range. FESEM is a microscope that works with electrons (particles with a negative charge) instead of light. A FESEM is used to visualize very small topographic details on the surface or the entire or segmented objects. The field emission cathode in the electron gun of the scanning electron microscope provides a narrower probing beam at low and high electron energies, resulting in both improved spatial resolution and minimized sample charging and damage. Figure 2 shows the high resolution of the schematic and ZEISS SIGMA FE-SEM are used [15].



**Figure 2: High-Quality Imaging and Advanced Analytical Microscopy**

## 3. Results and Discussion

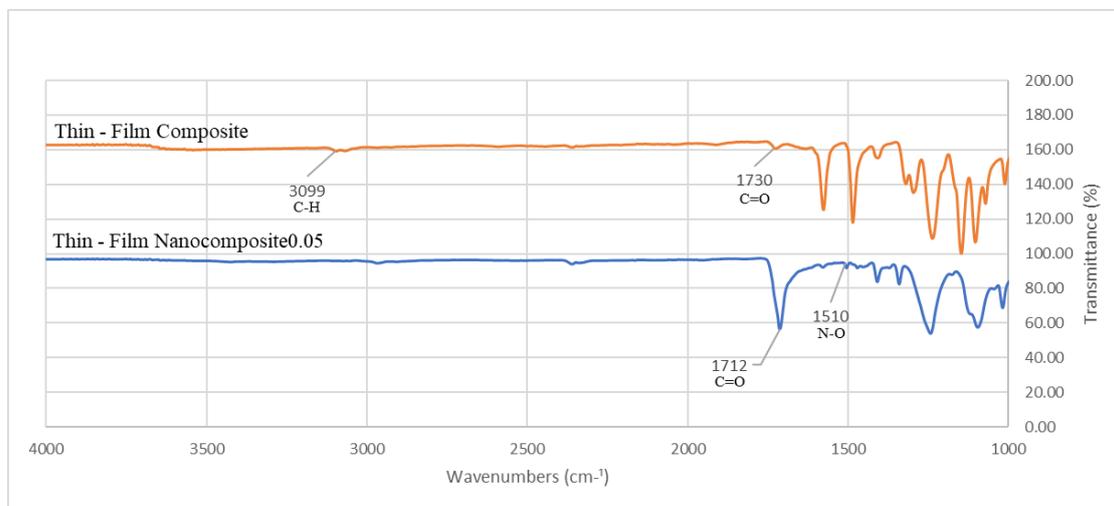
The results and discussion section presents data and analysis of the study. This section can be organized based on the stated objectives, the chronological timeline, different case groupings, different experimental configurations, or any logical order as deemed appropriate.

### 3.1 Morphology between TFC and TFN0.05 membranes

#### 3.1.1 FTIR

FTIR spectra of two composite membrane surfaces are shown in Figure 3. Overall, there is not much difference between the spectra of TFC and TFN membranes prepared. The results suggest that the incorporation of small quantities of inorganic nanofillers does not alter the spectra of the organic PA structure, indicating that dominant functional groups do not alter the spectra of the PA structure. The work of Barona et al. also reported similar observations [16] in which aluminosilicate single-wall nanotubes were incorporated in the PA layer of the composite membrane. In general, the peaks originating from the interfacially polymerized layer are TFC, and the first region that appears at peak  $3100 - 3000 \text{ cm}^{-1}$  are assigned to the C-H stretching with the medium appearance and the second region is represented by strongly defined peaks at  $1730 - 1715 \text{ cm}^{-1}$  is corresponded to C=O stretching. Region

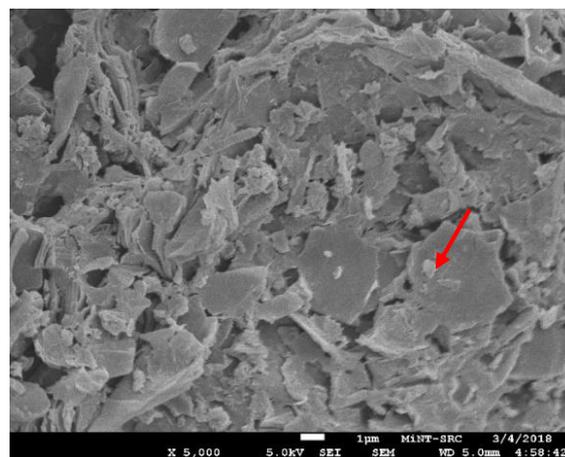
of TFN0.05 was identified by strong adsorption band at  $1712\text{ cm}^{-1}$  is due to the aliphatic ketone stretching, while the  $1510\text{ cm}^{-1}$  is nitro compound stretching. These analyses are characteristics of amides and appear at fixed positions with strong intensities, respectively.



**Figure 3: Comparison of FTIR TFC and TFN0.05 results**

### 3.1.2 FESEM

Figure 4 shows an image of the FESEM surface of Functionalized Graphene Oxide that shows the highly wrinkled structure of GO in comparison to TFN0.05. It has been reported that highly wrinkled reduced graphene oxide nanosheets are more sensitive and show better recovery ability. Figure 5 shows the top surface of both prepared TFC membrane (a) and TFN membrane (b), respectively. The top surface of the PA TFC membrane shows a granular structure which is a typical structure of the PA membrane prepared using the IP process [17]. Meanwhile, it is shown that the *f*-GO can be observed on top of the PA of TFN membranes (Figure 5(b)), respectively.



**Figure 4: FESEM image of GO**

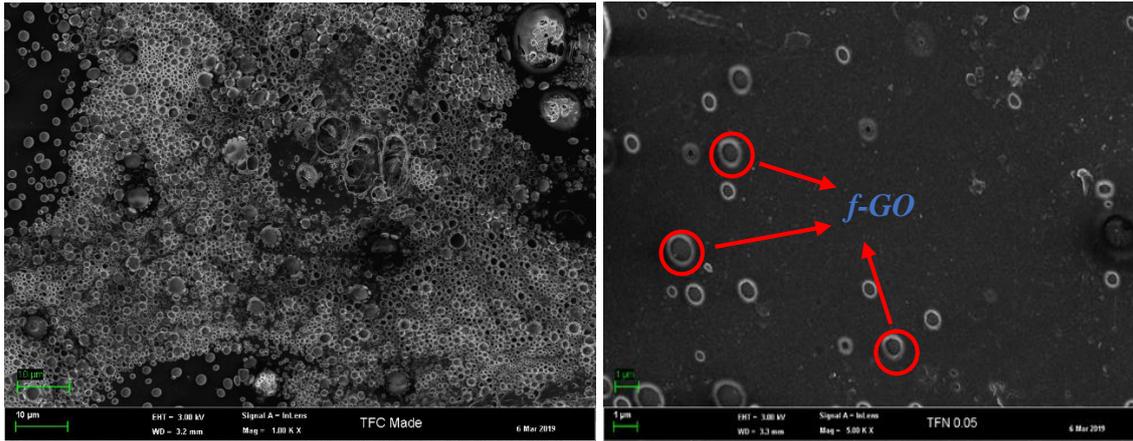


Figure 5: (a) FESEM image of TFC membrane; (b) FESEM image of TFN0.05 membrane

### 3.1.3 Cross-sectional of TFC and TFN0.05 membranes

The FESEM images in Figure 6 indicate the typical characteristics of interfacially polymerized membranes consisting of granular structures. As we can see, Fig. 6(a) and (b) show the different thickness of the PA layer which is TFC is 3.4 µm and the TFN layer is at 1.5 µm. The difference between both membranes is 1.5 µm. The thickness of the PA layer was reduced when the *f-GO* nanoparticles were added during the formation of composite membranes. It has been acknowledged that GO is hydrophilic. Therefore, when *f-GO* was added during the interfacial polymerization process, the *f-GO* would reduce the penetration of PIP to be in contact with TMC, resulting in more thinner layer of PA.

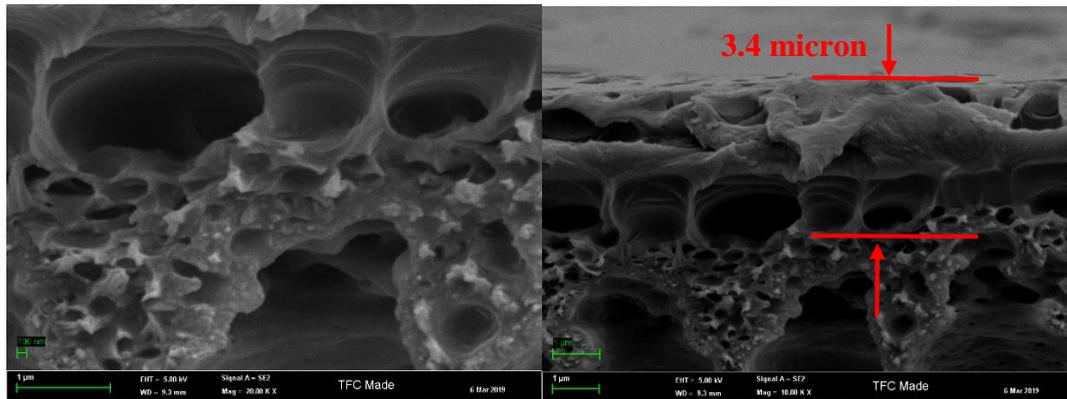


Figure 6: (a) FESEM images of the top surface and cross – section of TFC

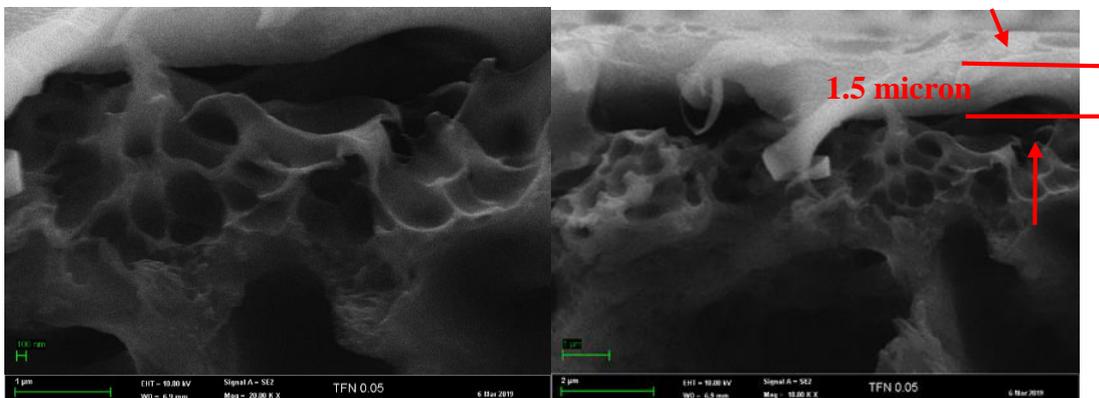


Figure 6: (b) FESEM images of the top surface and cross-section TFN0.05

### 3.1.4 Separation performance of TFC and TFN0.05 membranes

Experimental data of flux and salt rejections of prepared composite membranes are outlined in Table 2. With respect to water flux, it is reported that the flux increased two-fold for the TFN0.05 membrane compared to that of the pristine TFC membrane. The lowest flux reported for the TFC membrane is most likely due to the significant increase in PA thickness. Furthermore, the rejection of both Na<sub>2</sub>SO<sub>4</sub> and MgSO<sub>4</sub> remarkably increased upon the addition of *f-GO* nanoparticles.

**Table 2: Separation performance of TFC and TFN0.05 membrane**

Membrane	Water Flux (LMH)	MgSO <sub>4</sub> Rejection (%)	Na <sub>2</sub> SO <sub>4</sub> Rejection (%)
TFC	86.03 ± 0.45	41 ± 8.5	90 ± 0.5
TFN0.05	167.52 ± 0.67	90.7 ± 1.4	98 ± 1.2

## 4. Conclusion

TFN membranes have received considerable attention recently due to their improved physicochemical properties such as hydrophilicity, mechanical stability, and thermal resistance. Physical and chemical experiments were performed and analyzed on the materials of TFC and TFN0.05. The results of the TFN0.05 obtained are suitable for membranes, especially in desalination applications. Other than that, the characterization properties of the membrane were also determined by the use of FTIR analysis. The layer thickness in the cross-sectional of the membrane was determined by the use of FESEM analysis together with morphology of the porous surface of the membrane. The data were obtained and it is concluded that the TFN0.05 membrane works best in the separation of Na<sub>2</sub>SO<sub>4</sub> and MgSO<sub>4</sub> salt. This is coinciding with the higher compatibility of polymer-coated nanoparticles with PA and can facilitate the sustainable improvement of the performance and properties of the TFN membranes developed.

## Acknowledgment

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