

# Preparation and Surface Morphology Control of Self-Assembled Graphene Oxide/Chitosan Composite Membrane

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## ABSTRACT

Graphene oxide (GO)/chitosan composite membrane with a thickness of several hundred nanometers was prepared through an interfacial self-assembly process. Thermogravimetric analysis (TGA), Fourier transform infrared (FTIR) spectra and X-ray photoelectron spectroscopy (XPS) were employed to study the interactions that induced the assembly of GO nanosheets and chitosan and identified that the results showed that the major interactions were from electrostatic interactions. The surface morphology of synthesized membrane can be further tuned by adjusting the concentration of the chitosan solution. This new method is very effective to improve the GO/chitosan composite membrane production and may promote its broad potential applications in battery industry and life sciences.

**KEYWORDS:** Graphene Oxide, Chitosan, Nano-Membrane, Self-Assembly.

## 1. INTRODUCTION

Membranes are fascinating and versatile functional materials with a wide range of potential applications in separation, catalysis, sensors and so on.<sup>1</sup> Compared to traditional synthetic methods, self-assembly techniques such as layer-by-layer (LbL) assembly, are convenient and effective to construct multilayer thin film with predesigned composition and versatile functions.<sup>2</sup> Various structures including films, fibers and capsules have been obtained by LbL assembly processes.<sup>3–7</sup>

Graphene oxide (GO) sheets as new two-dimensional (2D) material attract tremendous interests in the past decade. The abundant oxygen-containing groups on their basal planes and edges make them good candidate materials for electrostatic self-assembly like anionic polyelectrolytes. They showed great potentials as building blocks with various functions and/or structures.<sup>8–10</sup> Various types of GO based membranes have been produced through electrostatic self-assembly. For example, transparent thin film with low oxygen permeability was produced by alternatively depositing branched polyethylenimine (PEI)

and GO.<sup>11</sup> Conductive composite film, as efficient micro-electrodes for photodetector devices was obtained by a combination of LbL assembly of GO nanosheets and polyoxometalate clusters and subsequent UV reduction.<sup>12</sup> GO/chitosan composite layers with stacked structures were synthesized using chemically exfoliated GO sheets (with the lateral dimensions of  $\sim 1 \mu\text{m}$  and a thickness of  $\sim 1 \text{nm}$ ), and applied as antibacterial and flexible nanostructured templates in stem cell proliferation.<sup>13</sup>

Formation mechanism and interactions between building blocks are crucial to synthesize GO based materials with excellent performance. In order to optimize the design of GO paper, a semi-ordered accumulation mechanism for vacuum-assisted self-assembly was proposed.<sup>14</sup> The residual oxygen-containing groups on the reduced graphene oxide (rGO) were investigated through molecular dynamic simulations.<sup>15</sup> However, the electrostatic interactions between GO and polyelectrolytes and their self-assembly dynamics is seldom investigated, making it difficult to provide guidelines in the design of GO based composite materials, though they are widely produced in this way. Herein, we investigated the formation process of GO/chitosan nanomembrane through self-assembly at the air-liquid interface. Thermogravimetric analysis (TGA), Fourier transform infrared (FTIR) spectra and X-ray photoelectron spectroscopy (XPS) were employed

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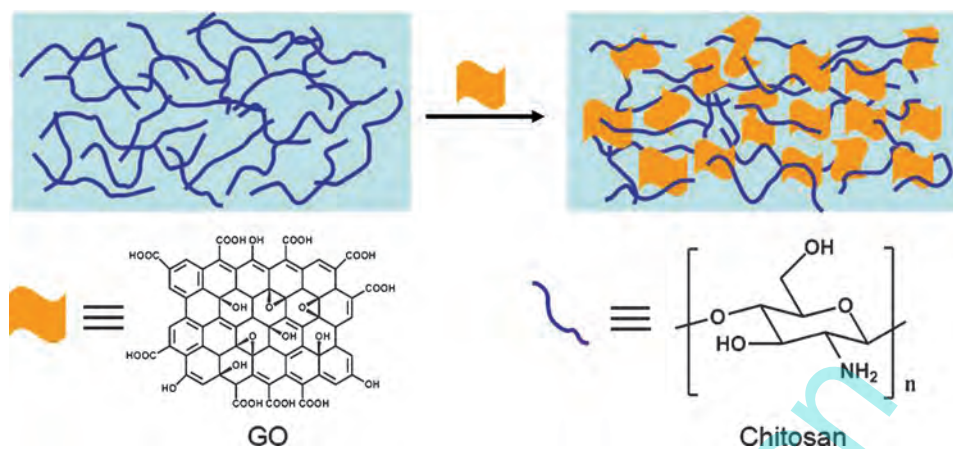


Fig. 1. Schematic representation of fabrication for GO-chitosan nanomembrane.

to study the interactions that induced the assembly of GO nanosheets and chitosan. Based on our findings, the surface morphology of the as-prepared membrane was further tuned by adjusting the concentration of chitosan. Our method is effective to improve the properties of GO/chitosan composite membrane and may potentially promote its applications in battery industry and biology fields.

## 2. EXPERIMENTAL DETAILS

### 2.1. Materials

Styrene (St, AR) was purchased from Alfa Aesar. *N,N*-dimethylaminoethyl methacrylate (DMAEMA, AR) was purchased from Energy Chemical. Chitosan (AR), acetic acid (AR) and toluene (AR) were purchased from Sinopharm Chemical Reagent. Graphene oxide sheets were prepared following a modified Hummer method. St and DMAEMA were purified over  $\text{Al}_2\text{O}_3$  column and then stored at low temperature prior to use. Other reagents were used as received without further purification.

### 2.2. Preparation of GO Sheets

GO was prepared following a modified Hummers' method.<sup>16</sup> In a typical procedure,  $\text{NaNO}_3$  (0.95 g) and

graphite (1.0 g) were added into 46 mL concentrated  $\text{H}_2\text{SO}_4$  (98%) under stirring. After 10 min, 6.0 g  $\text{KMnO}_4$  was added slowly. The mixture was then heated to 35 °C and stirred for 6 hours. Subsequently, 80 mL water was added dropwise under vigorous stirring, resulting in a quick rise of the temperature to ~80 °C. The mixture was further stirred at this temperature for 30 min. Afterwards 200 mL water and 6 mL  $\text{H}_2\text{O}_2$  solution were added in sequence to dissolve insoluble manganese species. The resulting graphite oxide suspension was washed repeatedly by a large amount of water until the pH of the solution reached a constant value at ~4.0, and finally the suspension was diluted to 600 mL with water. 200 mL of the diluted graphite oxide suspension was transferred into a 500 mL conical beaker, and the suspension was gently shaken in a mechanical shaker at a speed of 160 rpm for ~6 hours. To remove the small amount of unexfoliated particles, the resulting viscous suspension was centrifuged



Fig. 2. Photograph of a GO/chitosan composite membrane.

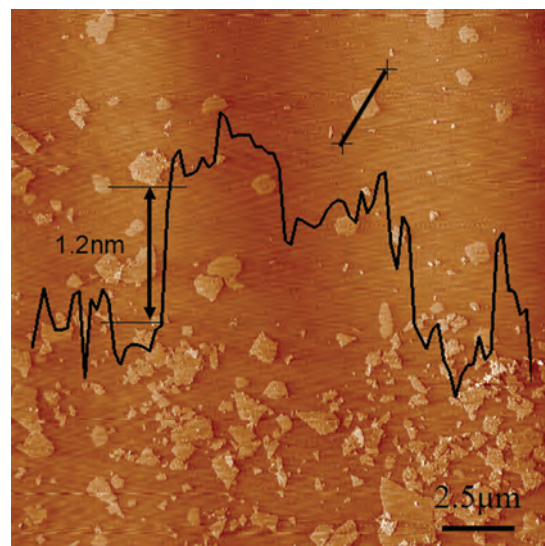


Fig. 3. AFM image of GO nanosheets and section curve of a single layer GO sheet.

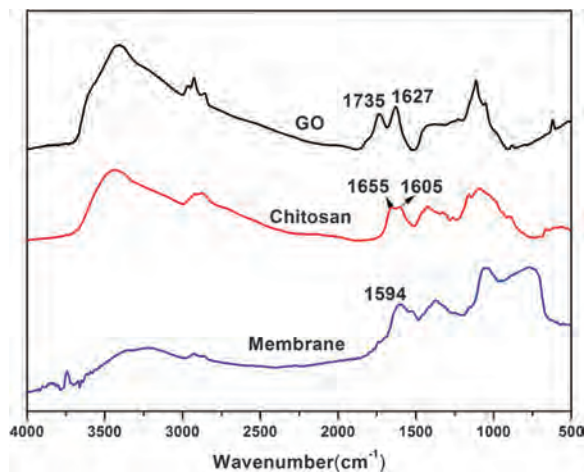


Fig. 4. FTIR spectra of GO, chitosan and GO/chitosan membrane.

Table 1. XPS analyses data of upper and lower surfaces of membrane.

Sample	Bonded NH <sub>2</sub> (%)	Free NH <sub>2</sub> (%)	N content (wt%)
Upper surface	51	49	3.43
Lower surface	28	72	5.45

at 2,000 rpm for 10 min, producing a brown, homogeneous colloidal suspension of GO sheets. The colloidal suspension could be further concentrated by centrifugation at 8,000 rpm.

### 2.3. Fabrication of GO Membrane

GO/chitosan membrane was prepared by an early reported approach with minor modifications.<sup>15,16</sup> Acetic acid of 0.5 wt% was added into the aqueous solution to dissolve chitosan and the pH value of the chitosan solution was adjusted to around 4.0. GO suspension (1 mg/mL in 9:1 DMF/water mixture) was gently injected onto the surface of the chitosan solution in glass Petri dishes using a plastic pipette as shown in Figure 1.

Chitosan solutions of various concentrations were tested to obtain GO/chitosan membrane with desired properties.

After loading, GO gradually spread and formed a thin film at the air-liquid interface. The membrane was transparent with a golden color (Fig. 2) and strong enough to be handled with tweezers. It could be further transferred to a silicon substrate and dried under ambient conditions to obtain a free-standing sheet.

With abundant hydroxyl and carboxyl groups on plane and edge, GO nanosheets behave like negatively charged polyelectrolytes that can interact with positively charged polyelectrolytes such as chitosan.<sup>17</sup> When mixing the GO suspension and chitosan solution, flocculation appeared immediately. However, no obvious changes were observed when GO solution is mixed with solution of negatively charged polyelectrolytes, such as poly(acrylic acid) (PAA). This suggests that the composite membrane is formed through the electrostatic interactions between GO and chitosan.

### 2.4. Characterization

Atom force microscopy (AFM) images were performed on a CSPM 5500 scanning probe microscope system in the tapping mode. Scanning electronic microscopy (SEM) measurements were performed on a Hitachi S4800 field-emission SEM system. Fourier transform infrared (FTIR) spectra were recorded on a Thermo Nicolet 6700 spectrometer. Thermogravimetric analysis (TGA) was conducted with a Mettler TG/DSC instrument with a heating rate of 10 °C/min under N<sub>2</sub> atmosphere.

## 3. RESULTS AND DISCUSSION

### 3.1. Characterization of GO

The obtained GO sheets can be dispersed uniformly in water for a long time, which demonstrates that graphite is successfully exfoliated and the hydrophilic groups are attained on exfoliated sheets. The presence of hydrophilic groups including hydroxyl, epoxy, carbonyl and carboxyl groups was verified by FTIR spectra (Fig. 4). The thickness of GO sheets was determined to be 1.2 ± 0.2 nm, and their sizes ranged from 1 to several micrometers (Fig. 3). Compared with graphene of a thickness of 0.34 nm,

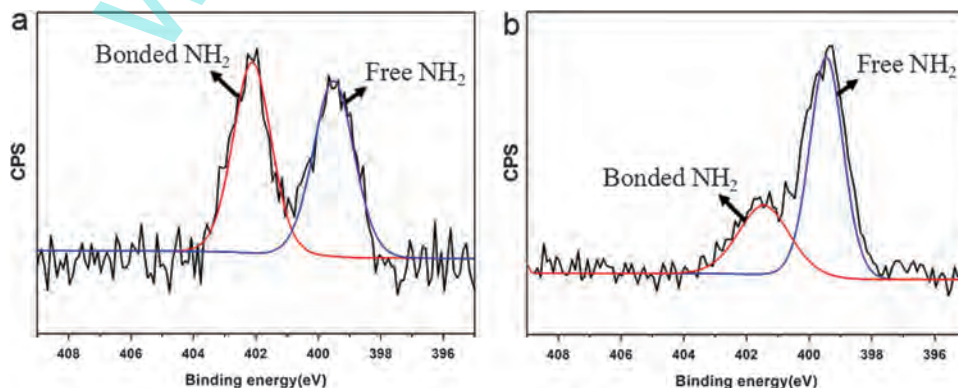


Fig. 5. N1s spectra of the (a) upper surface and (b) lower surface of GO/chitosan membrane.

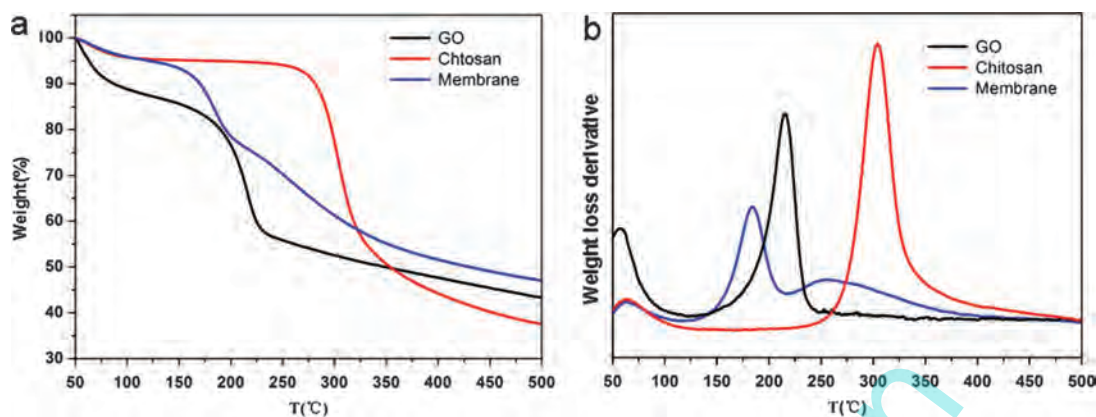


Fig. 6. (a) Thermogravimetry (TG) and (b) differential thermogravimetry (DTG) curves of GO, chitosan and GO/chitosan membrane.

the increased thickness of GO is ascribed to oxygen-containing groups on plane and the value tells that single layer GO sheets are obtained.

### 3.2. Interactions Between GO and Chitosan

In order to investigate the interactions between chitosan and GO sheets, FTIR was performed. As shown in Figure 4, spectrum of GO shows the stretching vibration of C=O and C=C at about  $1735\text{ cm}^{-1}$  and  $1627\text{ cm}^{-1}$ , respectively.<sup>19</sup> For chitosan, absorption bands at  $3432\text{ cm}^{-1}$  are attributed to stretching vibration of hydroxyl and amine groups, and the bands at  $1655\text{ cm}^{-1}$  and  $1605\text{ cm}^{-1}$  are assigned to the  $-\text{NH}-\text{CO}-$  and  $\text{NH}_2$

groups, respectively.<sup>14</sup> Compared with GO and chitosan, the characteristic peaks of C=O at  $1735\text{ cm}^{-1}$  almost disappears and a new peak appears at  $1594\text{ cm}^{-1}$ , in the spectrum of GO/chitosan membrane, indicating electrostatic interaction occurs between GO and chitosan.

X-ray photoelectron spectroscopy (XPS) was employed to further investigate formation of GO/chitosan membrane. The maximum detectable depth of XPS is about 10 nm, and the thickness of the composite membrane is about 600 nm. Therefore, both the upper and lower surfaces of the composite membrane can be characterized with XPS without much interference. The mass analyses for N on upper and lower surfaces are determined to be about

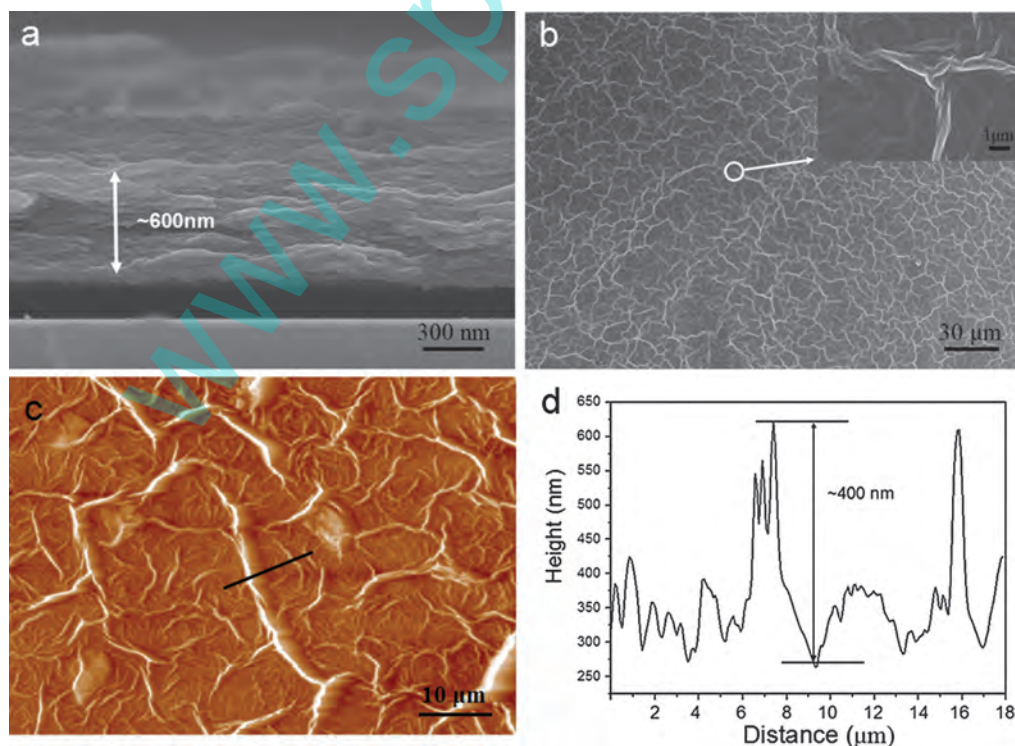
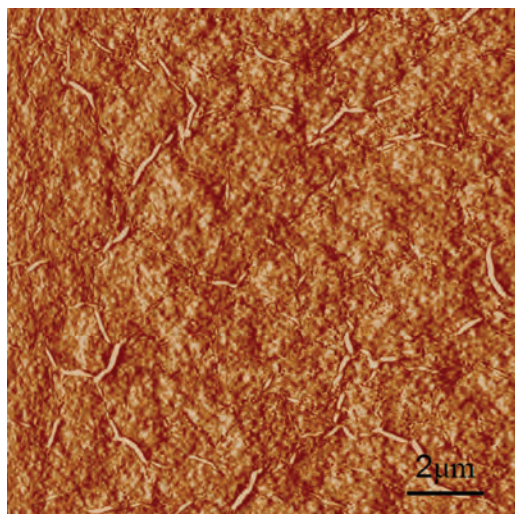


Fig. 7. SEM images of (a) cross-section and (b) top-view of GO/chitosan membrane. (c) AFM image and (d) the selected corresponding height profile of GO/chitosan membrane.



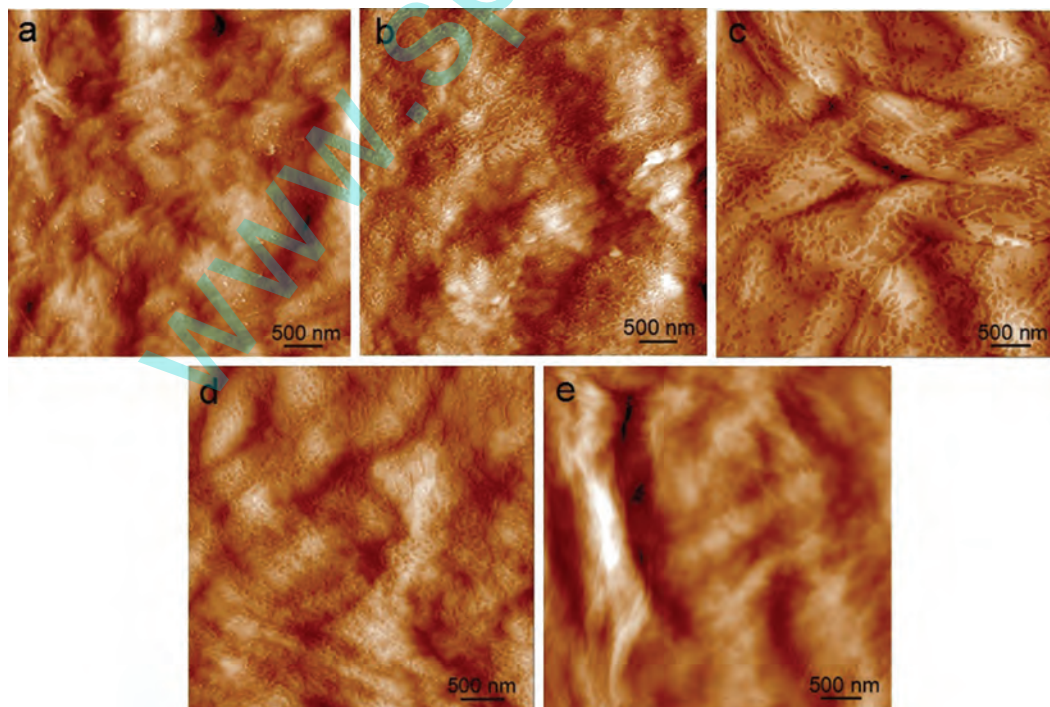
**Fig. 8.** AFM image of morphology for GO casted on silicon wafer.

3.43% and 5.45% (Table I), respectively, and it can be figured out content of chitosan on lower surface is about 20% higher than that on upper surface as *N* is only contained in chitosan. The N1s spectra of upper and lower surfaces are exhibited in Figure 5. The N1s spectra are deconvoluted into two component peaks. The peaks presented at about 402 eV and 399 eV in both spectra are assigned to bonded  $\text{NH}_2$  and free  $\text{NH}_2$ , respectively.<sup>20,21</sup> As mentioned above, the hydrogen bond between  $\text{NH}_2$  and OH is not the major interaction to the allied membrane.

Then the bonded  $\text{NH}_2$  groups are mainly attributed to those that electrostatically interact with COOH groups, which is consistent with our FTIR result. Additionally, more chitosan on lower surface than that on upper surface lead to that larger ratio of  $\text{NH}_2$  on upper surface complexes with COOH on GO. The quantitative result showed that the ratio of bonded  $\text{NH}_2$  on lower surface is only 28% (Table I), which is much lower than that of the upper surface (51%). This directly confirms that more  $\text{NH}_2$  groups on the upper surface interact with the oxygen-containing groups of GO. The XPS results suggest chitosan gradually spreads to the upper surface by penetrating into the gaps among GO sheets and complexes with GO. Therefore, electrostatical interactions between chitosan and GO sheets are the major interactions during the composite membrane formation.

### 3.3. Thermal Behavior of Composite Membrane

The thermal behavior of the membrane was investigated by Thermogravimetric analysis (TGA). As shown in Figure 6, there are two weight loss stages in the TG curve of GO/chitosan membrane, one at about 180 °C is attributed to chemical water loss of electrostatically bonded  $\text{NH}_2$  and COOH,<sup>18</sup> and the other one is related to thermal degeneration of the composite membrane. The degeneration temperature of the membrane is between those of GO and chitosan, which implies strong intermolecular interactions between GO and chitosan.



**Fig. 9.** AFM images of upper surfaces of GO/chitosan membranes prepared from chitosan solution with concentration of (a) 1 mg/mL, (b) 4 mg/mL, (c) 7 mg/mL, (d) 10 mg/mL and (e) 15 mg/mL, respectively.

### 3.4. Characterization and Regulation of Surface Morphology

In order to investigate the structure and morphology of the as-prepared membrane, scanning electronic microscope (SEM) and atom force microscope (AFM) were performed. As shown in Figure 7(a), GO sheets are closely packed and stacked in lateral fashion. The surfaces of GO sheets are rough due to the adsorption of chitosan. The thickness of the composite membrane is determined to be about 600 nm. SEM image of top-view of the composite membrane shows many wrinkles are highly crumpled to form some fiber-like structures (Fig. 7(b)), and these fibers are crossed and disperse uniformly on the whole surface of membrane. Compared with GO flakes which were casted onto silicon wafer (Fig. 8), the “fibers” of GO/chitosan membrane are much more crumpled which can ascribe to the interactions between chitosan and GO. The AFM image exhibits that there are different levels of wrinkles dispersing uniformly on the surface of membrane which is consistent with SEM results. The height of these wrinkles ranges from several tens to hundreds of nanometers (Fig. 7(d)).

The distinct raised structures on the upper surface can be tuned by adjusting the concentrations of the chitosan solution. Chitosan solutions with concentrations of 1 mg/mL, 4 mg/mL, 7 mg/mL, 10 mg/mL and 15 mg/mL were employed as underlying subphase in the preparation of composite membranes. When the concentration of chitosan was 1 mg/mL, no obvious raised structures were observed (Fig. 9(a)). When the concentration increased to 4 mg/mL, there were many distinct raised structures with an average size of dozens of nanometers on the upper surface, and the raised structures were isolated to each other like islands in the sea (Fig. 9(b)). The area of raised structures continuously increased and the isolated raised structures merged when the concentration increased to 7 mg/mL (Fig. 9(c)). As concentration reaches 10 mg/mL, the raised area further increased (Fig. 9(d)), and some textile-like structures were observed when the concentration reached 15 mg/mL (Fig. 9(e)). Since GO sheets are rigid and their conformations can't be changed like chitosan, the raised structures on upper surface are formed by chitosan molecules that penetrated through interspace between GO sheets to the upper surface. When the concentration of chitosan is low, GO is excessive and chitosan molecules are complexed when penetrating to surface. There is not enough chitosan to form raised structures on the upper surface. As the concentration of chitosan increases, more chitosan reaches the upper surface and stacks as raised structures, which increases with more concentrated chitosan solutions are used. With the concentration of chitosan further increasing, the excessive chitosan spreads on the upper surface and form textile-like structures. Therefore, the morphology of the upper surface can be regulated by adjust the concentration of chitosan. The TGA curves of membranes that

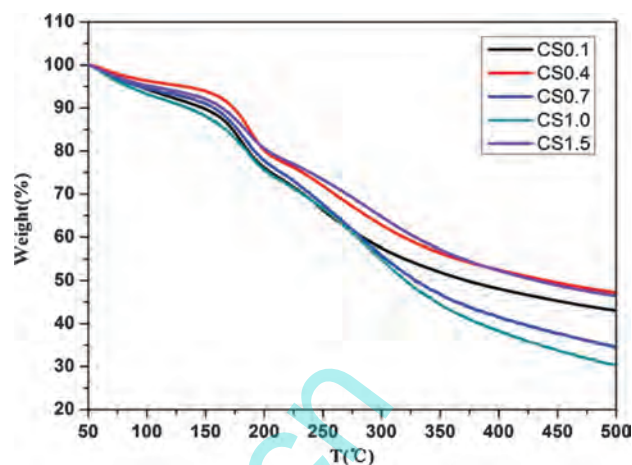


Fig. 10. Thermal gravimetry curves of GO/chitosan membrane prepared with chitosan solutions with different concentrations.

were prepared with different concentrations of chitosan look similar (Fig. 10), indicating that the concentration of chitosan does not influence the thermal behavior of the composite membrane within the investigation range.

## 4. CONCLUSION

In summary, we have investigated the formation of GO/chitosan composite membrane via self-assembly of GO sheets and chitosan at the air-liquid interface. The self assembly process is dominated by the electrostatic interactions between GO sheets and chitosan molecules. Wrinkles with heights ranging from tens to hundreds of nanometers are widely distributed on the upper surface of GO/chitosan membrane, and the raised structures on the wrinkles can be tuned by adjusting concentrations of the applied chitosan solution. Our findings may benefit the further study of interactions between GO nanosheets and polyelectrolytes and help design and produce composite membranes with desired structures and functions.

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