


Nanoscopic Roughness Characterization of Chitosan with Buried Graphene Oxide for Fuel Cell Application [†]

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Abstract: The combination of ecologically acceptable polysaccharide (chitosan) and graphene oxide (GO) nanoparticles was used to produce the cell membrane for a direct alkaline ethanol fuel cell (DAEFC). Due to its great power efficiency and minimal influence on the environment, this kind of fuel cell has a lot of potential uses. Recently, the performance of polymer-based DAEFC was significantly improved by the use of graphene. Since the roughness plays an important role in the charge transfer, herein we present our study of the change in the roughness of GO-blended chitosan using different preparation methods and different concentrations of GO.

Keywords: AFM; chitosan; graphene oxide; fuel cells; membrane; roughness



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1. Introduction

The development of fossil fuel alternatives to be environmentally friendly is a crucial topic for researchers. Therefore, researchers are working, on one hand, to find the functional material that has the ability to generate and/or convert energy and, on the other hand, to be sustainable and provide clean energy. A fuel cell is a device that converts energy from chemical to electrical through the oxidation of hydrogen with high conversion efficiency [1]. There are various types of fuel cells, in this work we are interested in studying the anion exchange membrane (AEM) fuel cell due to its numerous advantages [2–5]. AEMs are solid electrolytes that allow the conduction of carbonate and hydroxide anions. The presence of cationic groups on the backbone of the polymers causes the conduction process. Chitosan (CS), a member of a broad polysaccharide group of natural polymers, is among the most promising materials for this purpose, which is consolidated by its abundance [6]. CS consists of 2-amino-2-deoxy-(1,4)—D-glucopyranose units and is derived mostly from the exoskeletons of crustaceans (e.g., crabs and shrimps) and fungus. The advantages of using membranes that are CS-based are their nontoxicity and stability both chemically and thermally [7]. These advantages make CS-based membranes a potential candidate for alkaline alcoholic fuel cells.

Graphene oxide (GO) is a nanostructured sheet made of graphite. GO is attributed to having oxygenic functional groups (e.g., hydroxyl, carboxylic, and epoxy groups), which make it highly resistant to alkalis. The oxygenic groups make GO a good filler material which controls the anion transfer across the polymer.

Roughness is one of the important topographical parameters that plays an important role in the conduction process due to its influence on the mass transfer of ions through the membrane [7–10]. The roughness of the chitosan is influenced by the preparation method and the filler type and its concentration.

In this work, we present our study of the surface roughness of a chitosan–graphene oxide mixture which is a potential candidate for a direct alkaline ethanol fuel cell membrane.

2. Materials and Methods

2.1. Materials

Chitosan (degree of deacetylation: 90%, molecular weight: 50–100 kDa) was purchased in powder form with particle size below 200 μm from Biolog Heppe GmbH, Germany. GO, magnesium hydroxide nanopowder ($\text{Mg}(\text{OH})_2$), sodium hydroxide (NaOH), hydrochloric acid (HCl), ethanol, and potassium hydroxide (KOH) were purchased from Sigma-Aldrich, Germany. All chemicals were used as received.

2.2. Method

First, the membrane material was prepared as a solution. The pristine or blended graphene oxide solutions were prepared as mentioned elsewhere [11]. In brief, CS was dissolved in MilliQ water and HCl at pH around 2 at room temperature. The solution was stirred for 3 h until it became homogeneous and transparent. Then, by adding water dispersion of $\text{Mg}(\text{OH})_2$ 1 wt% to chitosan solution, its pH was raised to the range between 6 and 6.2. The solution was diluted to a final 1 wt% of CS and 12.6 mM of $\text{Mg}(\text{OH})_2$.

A mixture of CS + $\text{Mg}(\text{OH})_2$ membranes and GO filler were prepared by dispersing a specified amount of filler in MilliQ water before adding to the CS solution, resulting in a final 0.01 wt% filler concentration, and stirred until a homogeneous dispersion was obtained. This dispersion was degassed in an ultrasound cleaning bath for 10 min.

For preparing the samples for roughness analysis, first square glass microscope slides ($2 \times 2 \text{ cm}^2$) were cleaned using acetone, ethanol, then MilliQ water. Then, the film was deposited on the slides by casting 300 μL of the solution either by spinning a single layer or a layer-by-layer deposition at 2000 rpm for 60 s.

Substitution of chloride ions on the quaternary ammonium side chains with hydroxide ions was achieved by immersing the dried membrane in a surplus amount of 1 M KOH for 48 h, followed by an additional 48 h of immersion in MilliQ water with frequent replacement of water, which aids in the removal of potassium hydroxide. Finally, the membranes were thoroughly dried in the air.

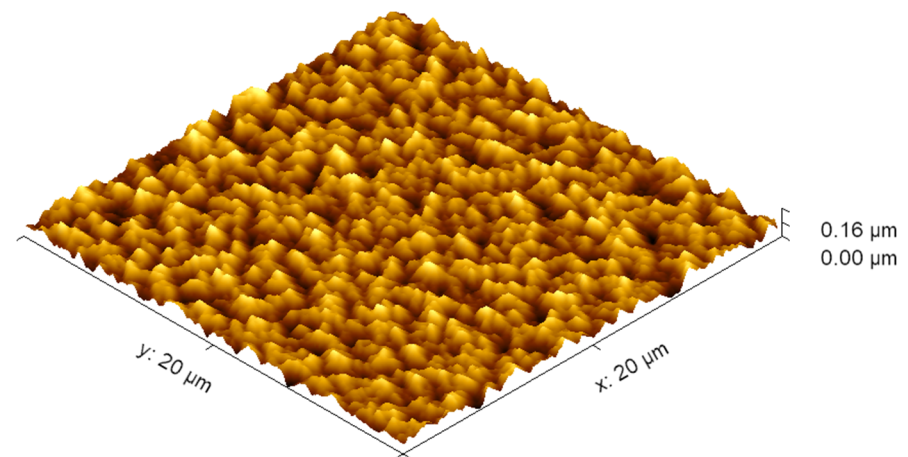
2.3. AFM Measurement

Two different samples of each pristine CS and CS blended with GO were prepared as mentioned above and scanned using APE Research SPM by operating it in AFM non-contact mode. The samples were scanned using a MikroMasch tip with a force constant of 40 N/m and 125 μm length. The samples were scanned in ambient at a scanning rate of 1 Hz with a scanning area of $20 \times 20 \mu\text{m}^2$. The images were collected, and statistical data were extracted from them as elaborated in our previous publications [12–16].

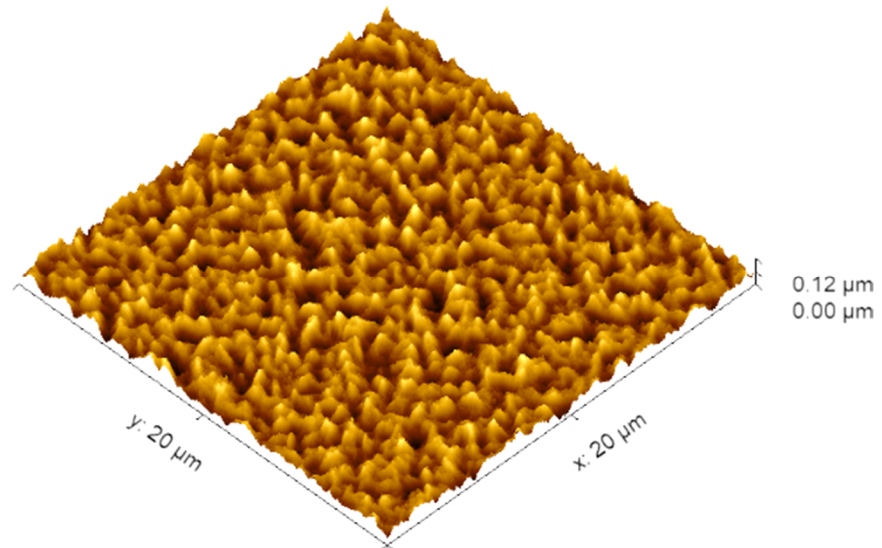
3. Results and Discussion

Figure 1 shows three-dimensional topography images of the selected samples' surfaces. It can be seen in Figure 1 that there is not much difference between the spin-coated pristine CS (Figure 1a) and CS with 0.01% GO (Figure 1b). Figure 1c represents the surface topography of CS-GO when it is deposited using the layer-by-layer method. By visual examination of the images, it can be inferred that the average height was reduced when GO was added to CS. In addition, the layer-by-layer method results in a modified morphology with reduced roughness.

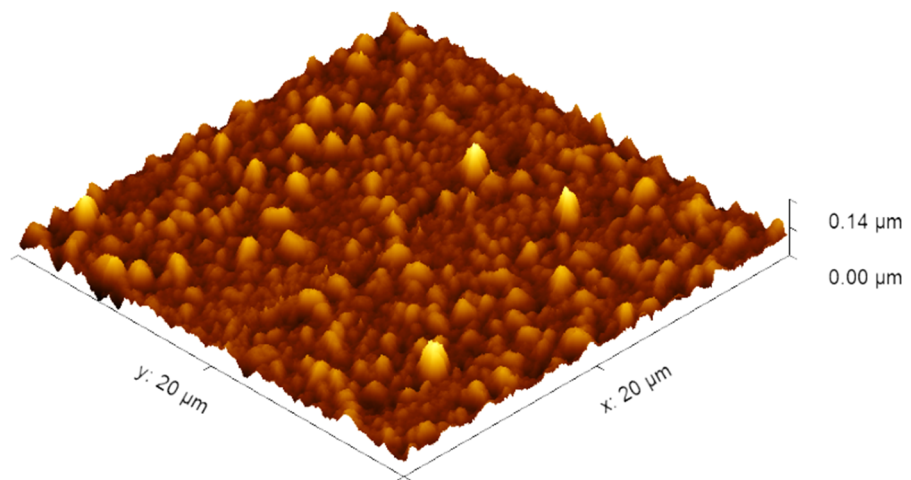
To get a deeper insight, the statistical data, namely average height and roughness averages, were calculated for all the topography images for the different samples and tabulated in Table 1. It can be inferred from the data in Table 1 that adding GO to CS reduces the average height; however, the roughness average did not show a critical change in the case of a single layer. Furthermore, the samples prepared using the layer-by-layer method exhibit a much lower average height and roughness.



(a)



(b)



(c)

Figure 1. Topography images of chitosan samples deposited on glass slides: (a) pristine chitosan (reference); (b) one layer of (0.01 wt% GO blended with chitosan); (c) three layers of (0.01 wt% GO blended with chitosan).

Table 1. Roughness and the average height of the samples.

Sample	Layers	Average Height (nm)	Roughness (nm)
CS (reference)	Single layer	70 ± 7	19 ± 3
CS +GO	Single layer	56 ± 1	17 ± 0.2
CS +GO	Layer by layer (3 layers)	40 ± 15	10 ± 6

4. Conclusions

The morphology of the chitosan material was studied after the addition of graphene oxide. The addition of graphene oxide reduced the surface roughness to 17 ± 0.2 nm in comparison to pristine chitosan which has a roughness average of 19 ± 3 nm. The roughness was further decreased to 10 ± 6 nm and the average height to 40 ± 15 nm while the average height of pristine chitosan was 70 ± 7 nm. It can be concluded that graphene oxide reduces the surface roughness and layer-by-layer is better than spinning a single layer of the film.

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