Preparation and Characterization of a Novel Sulfonated Titanium Oxide Incorporated Chitosan Nanocomposite Membranes for Fuel Cell Application

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Abstract: In this study, nano-TiO$_2$ sulfonated with 1,3-propane sultone (STiO$_2$) was incorporated into the chitosan (CS) matrix for the preparation of CS/STiO$_2$ nanocomposite membranes for fuel cell applications. The grafting of sulfonic acid (–SO$_3$H) groups was confirmed by Fourier transform infrared spectroscopy, thermogravimetric analysis and energy-dispersive X-ray spectroscopy. The physicochemical properties of these prepared membranes, such as water uptake, swelling ratio, thermal and mechanical stability, ion exchange capacity and proton conductivity, were determined. The proton conducting groups on the surface of nano-TiO$_2$ can form continuous proton conducting pathways along the CS/STiO$_2$ interface and thus improve the proton conductivity of CS/STiO$_2$ nanocomposite membranes. The CS/STiO$_2$ nanocomposite membrane with 5 wt% of sulfonated TiO$_2$ showed a proton conductivity (0.035 S·cm$^{-1}$) equal to that of commercial Nafion 117 membrane (0.033 S·cm$^{-1}$). The thermal and mechanical stability of the nanocomposite membranes were improved because the interfacial interaction between the -SO$_3$H group of TiO$_2$ and the –NH$_2$ group of CS can restrict the mobility of CS chains to enhance the thermal and mechanical stability of the nanocomposite membranes. These CS/STiO$_2$ nanocomposite membranes have promising applications in proton exchange membrane fuel cells.

Keywords: sulfonated TiO$_2$; chitosan; nanocomposite membrane; proton exchange membrane fuel cell

1. Introduction

Increasing environmental pollution and depleting natural resources have emphasized the need for clean and sustainable energy [1–5]. One of the most effective methods for this purpose is the conversion of chemical energy into electrical energy [6–9]. In recent years, proton exchange membrane fuel cells (PEMFCs) have gained much consideration in energy fields owing to their high effectiveness and environmental friendliness [10–13]. Perfluorosulfonic polymer-based membranes such as Nafion have high proton conductivity and notable mechanical and chemical stability due to the particular structure of Nafion [14–17]. However, the practical applicability of Nafion is restricted by its high price and sudden decline in proton conductivity at temperatures higher than 100 °C. Chitosan (CS) has the advantages of low cost, hydrophilicity and environmental benefits [18–20], making it attractive for various applications such as food packaging, drug delivery and...
PEMs [21,22]. However, its proton conductivity is much lower than that of Nafion, which represents a major hindrance to the applications of CS-based membranes.

Organic/inorganic composites are composed of the polymer matrix and inorganic fillers [23], and they have been widely utilized in different fields such as ultrafiltration, pervaporation, dye-sensitized solar cells, lithium-ion batteries and biosensors [24–28]. Various inorganic fillers, such as TiO$_2$, zirconium oxide, halloysite, and graphene oxide, can be introduced into the polymer matrix for the fabrication of PEMs [29–32], which can improve the mechanical and thermal stabilities of PEMs, as well as the proton conductivity in some cases [33]. Incorporating acid-grafted inorganic fillers into the polymer matrix can increase the proton conductivity and interfacial compatibility of the composite membranes [34–38]. TiO$_2$ as inorganic fillers has been widely used in photo-catalysis, biosensors and solar cells due to its hydrophilic nature and ultraviolet resistance [39–43]. Earlier reported literature narrates that incorporating TiO$_2$ as an inorganic filler has a positive effect on the thermal and mechanical stabilities of the resultant membranes [44,45]. Slade et al. reported that the addition of TiO$_2$ in Nafion 1100 membranes improved the mechanical stability and ion exchange capacity of the Nafion 1100 membranes [46]. Similarly, the hygroscopic nature of TiO$_2$ aids in water management within membranes and subsequently improves proton conductivity [47].

In this study, a novel sulfonated TiO$_2$ was prepared and embedded into the CS matrix to prepare CS/STiO$_2$ nanocomposite membranes. These sulfonated TiO$_2$ particles and CS/STiO$_2$ nanocomposite membranes were characterized by Fourier transform infrared (FTIR) spectroscopy, energy-dispersive X-ray (EDX) spectroscopy, X-ray diffraction (XRD) analysis, scanning electron microscopy (SEM), and thermogravimetric analysis (TGA). The effects of sulfonated TiO$_2$ particles (STiO$_2$) on the physicochemical properties of CS/STiO$_2$ membranes, including water uptake, area swelling, ion exchange capacity (IEC), and proton conductivity, were investigated. The interfacial interactions among the –SO$_3$H groups of STiO$_2$ and the –NH$_2$ groups of CS could offer uninterrupted proton conducting pathways, making it possible to enhance proton conductivity along with the mechanical stability of membranes.

2. Experimental

2.1. Materials and Chemicals

CS with a deacetylation value of 80% and rutile-type titanium dioxide powder with a particle size of 80 nm were purchased from Aladdin Chemical Reagent Co., Shanghai, China. Acetic acid (99%), sulfuric acid (98%) and 1, 3-propane sultone were purchased from Macklin Biochemical Co., Ltd., (Shanghai, China). Absolute ethyl alcohol ≥99.8% and deionized water were used during the experiments.

2.2. Sulfonation of Nano-TiO$_2$

One gram TiO$_2$ was dispersed in 22 mL of a mixture solution consisting of 1, 3-propane sultone and toluene with a volumetric ratio of 1: 11, and was refluxed at 110 °C for 24 h (Figure 1). The sulfonated titania (STiO$_2$) was centrifuged, washed several times with water and absolute ethyl alcohol, and then dried at 80 °C for 24 h.

2.3. Preparation of CS/STiO$_2$ Nanocomposite Membranes

CS/STiO$_2$ nanocomposite membranes with different STiO$_2$ contents were fabricated as follows: 1.5 g of CS was dissolved in 2.0 wt% aqueous acetic acid solution under constant stirring, and then a certain amount of STiO$_2$ was ultrasonically distributed in 2 wt% acetic acid solution at 300 W and 40 Hz for 1 h. After that, the two mixtures were homogenously mixed at 80 °C for 1 h. After degassing, the homogenous mixture was cooled down without phase separation and sedimentation and poured in a clean glass plate. The contents of the glass plate were dried in an oven at 40 °C for 24 h, and the obtained membranes were cross-linked with 1 M H$_2$SO$_4$ solution for 48 h to obtain completely cross-linked membranes. Finally, the CS/STiO$_2$ membranes were thoroughly washed with deionized
water to remove the remaining H₂SO₄ and dried under vacuum at 25 °C for 24 h. The CS/STiO₂ nanocomposite membranes with 1 wt%, 3 wt%, 5 wt% and 7 wt% of STiO₂ were named as CS/STiO₂-1, CS/STiO₂-3, CS/STiO₂-5 and CS/STiO₂-7, respectively. For comparison, pure CS membranes were prepared by the same method without the addition of STiO₂. The thickness of the prepared membranes had range from 20–25 μm.

2.4. Characterization

The FTIR spectra of STiO₂ and CS/STiO₂ nanocomposite membranes were recorded in transmittance mode at a scan rate of 4 cm⁻¹ and a wavelength of 500–4000 cm⁻¹ at room temperature using a Nicolet 6700 FTIR spectrometer (Thermo Scientific, Waltham, MA, USA). The phase identification and crystalline structure of CS/STiO₂ nanocomposite membranes were determined using a Rigaku D/max diffractometer, Rigaku, Tokyo, Japan (2550 VB/PC; CuKα; λ = 0.154 nm radiation) at an operating current and voltage of 40 mA and 40 kV respectively in the 2θ range from 5° to 80° at a scanning speed of 50 min⁻¹. The cross-sectional morphologies of CS/STiO₂ nanocomposite membranes were characterized by SEM (FE-S4800, Hitachi, Tokyo, Japan) equipped with an EDX spectroscope at an accelerating voltage of 200 kV. Prior to analysis, all samples were fractured in liquid nitrogen and sputtered with a thin gold layer. TGA was performed using a TA 50 thermogravimetric analyzer (Shimadzu, Tokyo, Japan) under nitrogen atmosphere at a rate of 10 °C min⁻¹ from 25 °C to 700 °C. The mechanical properties were determined using a MTS E43 universal testing machine (MTS, Shanghai, China) according to Chinese standard GB.T.1040.3 at an initial speed of 2 mm/min at room temperature.

2.5. Measurement of Water Uptake and Swelling in Dimension

The water uptake of CS/STiO₂ nanocomposite membranes was measured by the weight difference between dry membranes (Wdry) and membranes dipped in water for 24 h at room temperature (Wwet). In order to measure swelling in dimension, a piece of dry CS/STiO₂ nanocomposite with an area of 2.0 cm × 1.0 cm (Adry) was immersed in water for 24 h at room temperature and then its area was re-measured (Awet, cm²), as shown in Equation (2).

\[
\text{Water Uptake (\%)} = \frac{\text{Wwet} - \text{Wdry}}{\text{Wdry}} \times 100 \% \quad (1)
\]

\[
\text{Swelling in dimension (\%)} = \frac{\text{Awet} - \text{Adry}}{\text{Adry}} \times 100 \% \quad (2)
\]

2.6. Calculation of Ion Exchange Capacity (IEC)

The IECs of CS/STiO₂ nanocomposite membranes were calculated by classical acid-base titration method. A pre-weighted membrane was dipped in saturated 2.0 M NaCl solution for 48 h to achieve complete exchange of H⁺ with Na⁺. The solution was then
titrated by 0.01 M NaOH solution using phenolphthalein as the indicator at room temperature. The IEC value was calculated from Equation (3).

\[
\text{IEC (mmol/g)} = \frac{0.01 \times 1000 \times V_{\text{NaOH}}}{W_{\text{dry}}}
\]

(3)

where \(V_{\text{NaOH}}\) is the volume (mL) of the NaOH solution, and \(W_{\text{dry}}\) is the weight of the dry membrane.

2.7. Measurement of Proton Conductivity

The proton conductivity of CS/STiO2 nanocomposite membranes was measured by AC impedance spectroscopy on an electrochemical workstation (PARSTAT 2273 AMETEK, Inc., Berwyn, PA, USA) at a frequency of 1 Hz–106 Hz and an oscillating voltage of 20 mV. Before analysis, all nanocomposite membranes were dipped in 0.2 M \(\text{H}_2\text{SO}_4\) for 24 h. The hydrated membranes (2 cm \(\times\) 0.5 cm) were fitted in among the two electrodes of the polytetrafluoroethylene (PTFE) mould at room temperature with 100% RH. The proton conductivity was calculated from Equation (4).

\[
\sigma = \frac{L}{RA}
\]

(4)

where \(L\) (cm), \(A\) (cm\(^2\)) and \(R\) (\(\Omega\)) are the thickness, area and resistance of the membrane, respectively.

3. Results and Discussions

3.1. Characterization of STiO2

The surface modification of TiO\(_2\) was characterized by FTIR, TGA and EDX. The characteristic bands at 1631 and 3417 cm\(^{-1}\) in Figure 2a are due to the –OH bending and stretching vibration, respectively. STiO2 shows two new bands at 1044 cm\(^{-1}\) and 1206 cm\(^{-1}\), suggesting the successful grafting of sulfonic acid groups onto TiO\(_2\) with a significant reduction in hydroxyl groups [44].

![Figure 2. FTIR (a) and TGA analysis of TiO2 and STiO2 particles (b).](image)

The TGA curve displays a three-stage weight loss process (Figure 2b and Table 1). The first stage is attributed to the evaporation of physically adsorbed water, while the second stage is due to the loss of organic matter. However, there is a negligible weight loss at above 400 °C. Upon further heating, the weight loss is related to the decomposition of grafted chains. Moreover, STiO2 shows a higher weight loss than TiO2, suggesting that STiO2 has abundant sulfonic acid groups.

The EDX results (Table 2) show that pristine TiO2 has no sulfur, whereas STiO2 contains sulfur resulting from the reaction with 1,3-propane sultone, suggesting that sulfonic acid groups have been grafted onto the TiO2 surface.
Table 1. Thermal properties of TiO\(_2\) and STiO\(_2\) from TGA analysis.

| Samples | T5\(^{\circ}\) C | Char Yield (wt. %) |
|---------|------------------|--------------------|
|         | 500 \(^{\circ}\) C | 600 \(^{\circ}\) C | 700 \(^{\circ}\) C | 800 \(^{\circ}\) C |
| TiO\(_2\) | 420          | 92              | 91              | 91              | 90              |
| STiO\(_2\) | 256          | 89              | 88              | 88              | 88              |

Table 2. The atomic composition (%) of Ti, O and S in pristine TiO\(_2\) and STiO\(_2\).

| Serial No. | Ti  | O  | S  |
|------------|-----|----|----|
| TiO\(_2\)  | 22.71 | 77.29 | –  |
| STiO\(_2\) | 23.43 | 74.57 | 2.00 |

3.2. Structural Characterization of CS/STiO\(_2\) Nanocomposite Membranes

Figure 3 shows the FTIR spectra of CS/STiO\(_2\) nanocomposite membranes with different STiO\(_2\) contents. The characteristic peaks at 1650 cm\(^{-1}\) and 1558 cm\(^{-1}\) are attributed to the bending vibration of –NH\(_2\) group. The broad peak at 3426 cm\(^{-1}\) is attributed to –OH stretching [45]. The characteristic peaks at 2932 cm\(^{-1}\) and 1375 cm\(^{-1}\) are attributed to –CH stretching and –CH\(_3\) symmetric deformation, respectively [46]. After cross-linking with H\(_2\)SO\(_4\), the characteristic peaks at 1656 cm\(^{-1}\) and 1598 cm\(^{-1}\) are shifted to lower wave numbers, suggesting that the –NH\(_2\) of CS is protonated. This is endorsed to the shift of hydrogen bond structure and a change in intensity in CS molecules [47]. Enhancing the STiO\(_2\) content in nanocomposite membranes can shift the bands at 3600–3000 cm\(^{-1}\) and 1656–1592 cm\(^{-1}\) to lower wave numbers in CS/STiO\(_2\) nanocomposite membranes. This phenomenon corresponds to the formation of strong interfacial attractions among –SO\(_3\)H of STiO\(_2\) and –OH/–NH\(_2\) of CS molecules [48–52].

![Figure 3. The FTIR spectra of CS control and CS/STiO\(_2\) nanocomposite membranes.](image)

Strong intermolecular and intramolecular interactions within the chitosan molecule is the main reason for its high degree of crystallinity [53,54]. As the proton mobility and diffusion of water molecules in PEMs often take place in an amorphous phase, it is necessary to convert crystalline phase CS into a semi-crystalline or amorphous phase. The impact of STiO\(_2\) on the crystalline nature of CS was determined by XRD. The characteristic peak at 2\(\theta\) = 12\(^{\circ}\) depicts the hydrated crystalline section in the CS molecules, whereas that at 2\(\theta\) = 23\(^{\circ}\) depicts the amorphous section. However, incorporation of STiO\(_2\) results in a decreased peak intensity at 2\(\theta\) = 19\(^{\circ}\) and 2\(\theta\) = 23\(^{\circ}\) (Figure 4). The decrease in the
crystalline region is endorsed to the presence of hydrogen and electrostatic interactions between CS molecules and STiO₂ that can interfere with the order packing of the CS chain and subsequently diminish its crystalline region. The other peaks at \(2\theta = 27^\circ, 36^\circ, 44^\circ\) and \(56^\circ\) confirm the presence of rutile phase titania [55].

3.3. Thermal and Mechanical Stability of CS/STiO₂ Nanocomposite Membranes

The thermal stability of CS/STiO₂ nanocomposite membranes was determined from their TGA thermograms (Figure 6). Pure CS membrane shows a three-stage weight loss process. The initial stage at 30–200 °C is assigned to the evaporation of adsorbed water; the second one at 215–330 °C is due to the degradation of CS side chains; and the last one at 480–800 °C corresponds to the degradation of polymer backbone [49]. However, the incorporation of STiO₂ can retard the degradation of CS molecules and thus improves the thermal strength of CS/STiO₂ membranes, which is mainly due to the interfacial interactions (hydrogen bonding or electrostatic interactions) that can interfere with the order packing of CS chains and thus hinder the degradation of polymer backbone of CS molecules. The remaining weight of CS at 750 °C is 21.03%, and as the STiO₂ content increases from CS/STiO₂–1 to CS/STiO₂–7, the residual weight increases from 27.37% to 29.73%.
Moreover, it is clear that STiO\textsubscript{2} particles are homogeneously dispersed in the CS matrix with no obvious aggregation, which may be due to the strong electrostatic interactions between the polymer and nanofillers. This results in the formation of uninterrupted proton transfer pathways and consequently an improvement of the proton conductivity of CS/STiO\textsubscript{2} resultant membranes.

Figure 5. SEM images of cryo-fractured sections of CS control and CS/STiO\textsubscript{2} nanocomposite membranes with different STiO\textsubscript{2} contents. CS/STiO\textsubscript{2}–0 (a), CS/STiO\textsubscript{2}–1 (b), CS/STiO\textsubscript{2}–3 (c), CS/STiO\textsubscript{2}–5 (d) and CS/STiO\textsubscript{2}–7(e).

It is crucial for PEMs to have sufficiently high mechanical stability, which can have dramatic impacts on the durability of PEMFCs. Table 3 shows that all CS/STiO\textsubscript{2} nanocomposite membranes have higher tensile strength than pristine CS membranes (13.05 MPa). As the STiO\textsubscript{2} content increases from CS/STiO\textsubscript{2}–1 to CS/STiO\textsubscript{2}–7, the tensile strength increases from 17.84 MPa to 25.30 MPa, which is endorsed to (a) the increase of Coulombic interactions among the amine groups of CS and the –SO\textsubscript{3}H groups of TiO\textsubscript{2}; and (b) the hydrogen bonding between –SO\textsubscript{3}H of STiO\textsubscript{2} and –OH or –NH\textsubscript{2} groups of CS. These electrostatic interactions can restrict the mobility of CS chains and subsequently increase the tensile strength of CS/STiO\textsubscript{2} nanocomposite membranes. The –SO\textsubscript{3}H has a polar and ionic nature, and a proper concentration of sulfonic acid groups can result in the formation of ionic clusters in the CS matrix and consequently an increase in the tensile strength of CS/STiO\textsubscript{2} nanocomposite membranes. The CS/STiO\textsubscript{2}–7 nanocomposite membrane shows a higher tensile strength than the Nafion 117 membrane (23.6 MPa) [21,46]. The elongation at break (%) of the nanocomposite membranes is also improved compared with that of pure CS membrane. STiO\textsubscript{2} can halt the propagation of micro-cracks owing to the strong
interfacial interactions between STiO$_2$ and the CS matrix, thus resulting in an enhancement of the elongation at break of all nanocomposite membranes.

![Figure 6. TGA curves of CS control and CS/STiO$_2$ nanocomposite membranes.](image)

**Table 3. Mechanical properties of CS control and CS/STiO$_2$ nanocomposite membranes.**

| Membranes      | Tensile Strength (MPa) | Elongation at Break (%) |
|----------------|------------------------|-------------------------|
| CS/STiO$_2$–0  | 13.05 ± 1.03           | 15.61 ± 6.98            |
| CS/STiO$_2$–1  | 17.84 ± 2.02           | 23.54 ± 2.22            |
| CS/STiO$_2$–3  | 21.32 ± 3.33           | 19.57 ± 4.20            |
| CS/STiO$_2$–5  | 23.27 ± 0.92           | 21.59 ± 5.70            |
| CS/STiO$_2$–7  | 25.30 ± 2.69           | 19.34 ± 4.35            |
| Nafion 117     | 27                     | –                       |

### 3.4. Water and Methanol Uptake, Dimensional Stability and IEC of CS/STiO$_2$ Nanocomposite Membranes

The hydrolytic stability of CS/STiO$_2$ nanocomposite membranes was measured to evaluate their applicability in PEMFCs. Water uptake is expected to have significant impacts on the mechanical characteristics and proton conductivity of polymer electrolyte membranes. The existence of water within the membrane can assist the dissociation of various functional groups that is essential to achieve high proton conductivity. However, unnecessary water uptake can lead to dimensional instability that can influence performance of membrane during fuel cell operation. The water uptake of pristine CS membrane is as high as 65% owing to the presence of hydrophilic –OH and –NH$_2$ of CS (Figure 7a). However, an increase in STiO$_2$ content results in a decrease of water uptake from 58% to 51%. The addition of STiO$_2$ rigidifies CS molecules, thus making it less capable of adsorbing solvent molecules [33]. The cumbic and hydrogen bonding interactions between the –SO$_3$H groups of STiO$_2$ and the –NH$_2$ and –OH groups of CS can also reduce the water adsorption capacity of CS/STiO$_2$ nanocomposite membranes. The incorporation of STiO$_2$ can hinder the mobility of CS chains and reduce water storing sites, which results in reduction of the water uptake of CS/STiO$_2$ nanocomposite membranes [56,57].
3.5. Electrochemical Characteristics of CS/STiO₂ Nanocomposite Membranes

Proton conductivity is mainly determined by water content, distribution of water molecules and the formation of ionic clusters within a PEM [58]. Theoretically, there are two mechanisms for proton transfer in a membrane, including the Vehicle mechanism whereby protons are transported in the form of hydrated hydrogen ions, and the Grotthuss mechanism whereby protons are transported from one carrier to the next through hydrogen bonding networks [59,60]. The CS membrane displays a proton conductivity of 0.011 S·cm⁻¹, which is in good agreement with an earlier report [57]. The proton conductivity of Nafion 117 (0.033 S·cm⁻¹) is used for comparison in this study [61].

Increasing the STiO₂ content from 1.0 to 7.0 wt% can increase the proton conductivity from 0.019 to 0.035 S·cm⁻¹, as presented in Figure 8. There are abundant sulfonic acid groups in the polymer matrix that can offer extra proton hopping sites. The homogeneous dispersion of STiO₂ can offer continuous proton conducting pathways through which protons can migrate rapidly. Increasing the STiO₂ content can also increase the number of ion-exchangeable sites per cluster to improve proton mobility. The generation of acid-base pairs at the CS/STiO₂ interface can also facilitate the protonation/deprotonation process. All of these could improve the proton conductivity of nanocomposite membranes. The CS/STiO₂–5 nanocomposite membrane shows a proton conductivity (0.035 S·cm⁻¹) equal to that of commercially available Nafion 117 membranes (0.033 S·cm⁻¹).

The methanol uptake is also an important feature for nanocomposite membranes for their use in PEMFCs. It is desirable for PEMs to have lower methanol absorption, as a high methanol uptake can lead to fuel crossover and thus reduce cell efficiency. Pure CS membrane shows a methanol uptake of 56 %. As the STiO₂ content increases from CS/STiO₂-1 to CS/STiO₂-7, the methanol uptake decreases from 46 % to 42 % (Figure 7b). The methanol uptake of PEMs depends greatly on the available space within membranes. Water is more polar than methanol, making it easier to access the hydrophilic domains in a membrane. As the STiO₂ content increases, the diffusion capacity of nanocomposite membranes for methanol is suppressed. Hence, the methanol uptake of the nanocomposite membranes decreases [56].

Swelling via hydration can cause dimensional instability in PEMs. The area swelling of CS control and CS/STiO₂ nanocomposite membranes are shown in Figure 7c. It is noted that the incorporation of STiO₂ results in decrease in both water uptake and area swelling of the nanocomposite membranes. The swelling of these CS/STiO₂ nanocomposite membranes can also be reduced, as STiO₂ can inhibit the swelling of the CS matrix. The CS control membrane shows an area swelling of 60%, whereas that of the CS/STiO₂–7 membrane is significantly reduced to 42%.

The number of ionizable hydrophilic functional groups in the membrane gives a reliable estimation of proton conductivity. Figure 7d shows that the CS membrane has an IEC value of 0.125 mmol g⁻¹. In comparison, increasing the STiO₂ content from CS/STiO₂–1 to CS/STiO₂–7 results in an increase of IEC value from 0.153 to 0.220 mmol g⁻¹, which is mainly attributed to the presence of SO₃H groups in the CS matrix.

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![Proton conductivity of CS control and CS/STiO₂ nanocomposite membranes.](image)

**Figure 8.** Proton conductivity of CS control and CS/STiO₂ nanocomposite membranes.

### 4. Conclusions

In this study, a novel one step approach is proposed for the preparation of STiO₂-CS/STiO₂ nanocomposite membranes fabricated by the solution casting method for PEMFC applications. These membranes showed lower water and methanol uptake and better dimensional stability than CS membranes. Their thermal and mechanical stabilities can be improved due to the inhibited mobility of CS chains. The CS/STiO₂–5 membrane showed a higher proton conductivity than the Nafion 117 membrane. These outcomes may probe a simple strategy for the fabrication of chitosan-based PEMs, which has a promising potential in the application of electrochemical devices.

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