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Ultrasonic irradiation to modify the functionalized bionanocomposite in sulfonated polybenzimidazole membrane for fuel cells applications and antibacterial activity

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ABSTRACT

In this article the new proton exchange membranes were prepared from sulfonated polybenzimidazole (s-PBI) and various amounts of sulfonated titania/cellulose nanohybrids (titania/cellulose-SO_3H) via ultrasonic waves. The ultrasonic irradiation effectively changes the rheology and the glass transition temperature and the crystallinity of the composite polymer. Ultrasonic irradiation has a very strong mixing and dispersion effect, much stronger than conventional stirring, which can improve the dispersion of titania/cellulose-SO_3H nanoparticles in the polymer matrix. The strong –SO_3H/–SO_3H interaction between s-PBI chains and titania/cellulose-SO_3H hybrids leads to ionic cross-linking in the membrane structure, which increases both the thermal stability and methanol resistance of the membranes. After acid doping with phosphoric acid, s-PBI/titania/cellulose-SO_3H nanocomposite membranes exhibit depressions on methanol permeability and enhancements on proton conductivity comparing to the pristine s-PBI membrane. The chemical structure of the functionlized titania was characterized with FTIR, and energy-dispersive X-ray. Imidazole and sulfonated groups on the surface of modified nanoparticles forming linkages with s-PBI chains, improved the compatibility between s-PBI and nanoparticles, and enhanced the mechanical strength of the prepared nanocomposite membranes. From SEM and TEM analysis could explain the homogeneous dispersion of titania/cellulose-SO_3H in nanocomposite membranes. Moreover, the membranes exhibited excellent antibacterial activities against *S. aureus* and *E. coli. A*.

1. Introduction

Nafion® at present is one of the most advanced commercially available membranes for direct methanol fuel cells (DMFC) [1]. However, Nafion® application in DMFC is still limited by high cost and methanol crossover. Improvements in properties of the polymer electrolyte membranes have been strongly related to the developments of high performance proton exchange membranes (PEM) for DMFC.

Polybenzimidazole (PBI) is one of the most studied materials for applications in proton exchange membrane fuel cell (PEMFC). As PBIs are basic polymers, acid doping in PBIs results in an increase both in their proton conductivities and thermal stability [2,3]. The effects of acid-doping levels, temperatures, and relative humidity on the proton conductivities of PBI membranes were studied [4–11].

The proton conductivities of acid-doped PBI membranes were also dependent to the doped acids in the order of H_2SO_4 > H_3PO_4 > $HClO_4$ > HNO_3 > HCl [12]. However, the acids doped in PBI membranes might leak in fuel cell applications. One promising approach to overcome this drawback was to covalently bond the acid groups, especially sulfonic acid groups, to the PBI chains [3,13–16]. The sulfonated PBI membranes showed relatively high proton conductivities comparing to the corresponding pristine PBI membranes. Modification of PEMs to improve their thermal and chemical stability and to depress their methanol crossover is a useful approach to improve their performance. These pore-filling membranes showed high mechanical strength and low methanol crossover. The plasma treatment on Nafion® surface could change its surface properties substantially with a methanol permeability reduction of 74% and without altering their bulk properties.

Organic–inorganic nanocomposites represent another useful approach to PEM modification [17–19]. It is widely acknowledged that there is a growing need for more environmentally acceptable processes in the chemical industry. This trend towards what has become known as ‘green chemistry’ or ‘sustainable engineering’ needs research on

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technologies that use preferably renewable raw materials, produce less waste and avoid the use of toxic and hazardous reagents and solvents [20].

Cellulosic materials have also shown some promising applications in the development of alternative energy sources. For example, nanoporous regenerated cellulose membranes have been used in place of proton-exchange membranes in microbial fuel cells [21]. Membranes formed from cellulose acetate and nitrates have also been used extensively in electroanalytical applications [22–24].

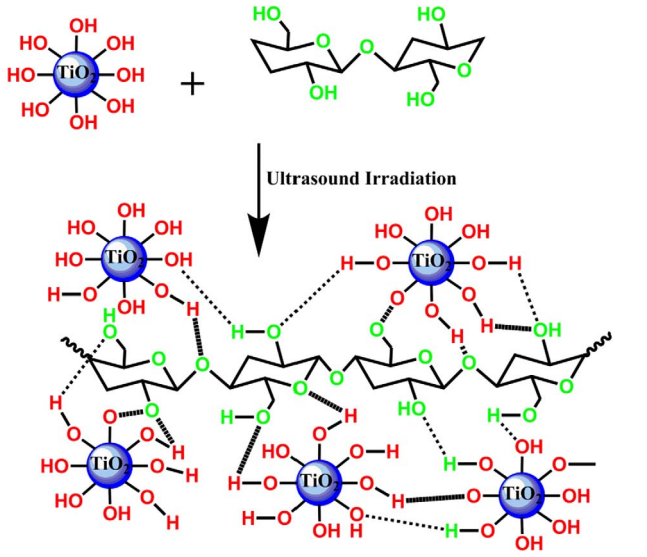
As a one-step facile wet chemical processing method, ultrasonication-assisted preparation (sonochemical processing method) is able to be operated at room temperature [25,26]. As an advanced preparation method, sonochemical approach concerns with understanding the effect of ultrasound irradiation and acoustic cavitation phenomenon on the formation of the final product expected [25]. Ultrasonication of a solution mixture of the precursors results in the initiation and enhancement of chemical activity of the reactant ions and clusters at low temperatures [27,28]. Sonochemical preparation method utilizes the acoustic cavitation phenomenon which includes the formation of the bubbles and their successive growth and implosive collapse in a mixture of the reactant ions and clusters [27]. As a mostly adiabatic process, this collapse of the grown bubbles leads to a massive energy build-up ensuing high pressures of about 2000 atm and very high temperatures more than 5273 K (5000 °C) in localized microscopic regions inside the sonicated solution mixture [29]. The benefits of the sonochemical processing method for obtainment of the oxide materials are high purity, narrow particle size distributions, controllable reaction conditions, ability to obtain nanoparticles with mostly uniform shape and rapid synthesis at much lower temperatures in contrast to other synthesis methods [27].

In this work, I reported the attempts on preparation of high performance s-PBI nanocomposite membranes for fuel cell application using sulfonated TiO_2/cellulose nanocomposites as nano-reinforcements. S-PBI nanocomposites membranes possessing non-sulfonated TiO_2/cellulose nanocomposites were also prepared to study the effects of sulfuric acid groups on the properties of s-PBI nanocomposite membranes. The new membranes were initially synthesized and then the identification of these membranes was performed. Identification of all membranes was carried out successfully. Then a series of process were performed to identify the properties of these membranes. Based on these data, each section briefly describes each one of membrane can be used under certain conditions and for specific applications. The sulfuric acid groups of TiO_2/cellulose formed ionic linkages with s-PBI chains, improved the compatibility between TiO_2/cellulose and s-PBI, and enhanced the mechanical strength of the PBI/TiO_2/cellulose bionanocomposite membranes. S-PBI/TiO_2/cellulose nanocomposite membranes exhibited depressions on methanol permeability and enhancements on proton conductivity comparing to the pristine s-PBI membrane, to promise their application potentials for fuels cells. Moreover, the membranes exhibited excellent antibacterial activities against S. aureus and E. coli. A.

2. Experimental

2.1. Materials

2,2-Bis(4-carboxyphenyl)hexafluoropropane, polyphosphoric acid (PPA), N,N-dimethylacetamide (DMAc), sulfuric acid, ethanol, diaminobenzidine reagent, dimethyl sulfoxide (DMSO), and 1,4-bis (hydroxymethyl) benzene (BHMB) were purchased from Aldrich (St. Louis, MO, USA) and used without any purification. Titania nanoparticles with an average particle size of about 10–15 nm were purchased from Neutrino Co (Tehran, Iran). The cellulose nanofibers (CNFs) used in this study were provided by the Institute of Tropical Forestry and Forest Products (INTROP), Malaysia, and were isolated from the kenaf bast fibers (Hibiscus cannabinus). The details of the CNFs isolation process



Scheme 1. Reaction Mechanism of Coupling Agent in Preparation of the modified TiO_2 nanoparticle.

are reported elsewhere. The selected fungus was a white rot fungus (Trametes versicolor), which was obtained from the National Collection of Biology Laboratory, University of Tehran, Iran. Glycerol, methanol, acetone, acetic anhydride (95%), pyridine, and malt extract agar (MEA) were purchased from the Merck Chemical Co., Germany. All the materials and solvents that were used were obtained from the suppliers without further purification.

2.2. Synthesis of titania/cellulose bionanocomposites with ultrasonic irradiation

Titania/cellulose bionanocomposites was performed using the reported method [30,31]. About 50 mg of TiO_2 nanoparticles were dispersed in a mixture of 40 mL of water/ethanol. The dispersion was homogenized by sonication for about 20 minutes. Then acetic acid (to keep the pH value at 4) was added. Finally, 20 mg of cellulose was added and the mixture was sonicated for 60 min. Titania/cellulose composites was filtered and then washed with ultrapure water (Scheme 1).

2.3. Surface-functionalization of titania/cellulose bionanocomposites

The reaction of titania/cellulose with glycidyl phenyl ether (GPE) was carried out as follows [34]. The titania/cellulose solution and GPE were mixed together. After adding 1000 ppm of $SnCl_2$ as a catalyst, the mixture was stirred at 130 °C for 6 h. The solvent was removed out with a rotary evaporator, and a condensed product (titania/cellulose-GPE) was obtained with centrifugation. The sulfonation on titania/cellulose -GPE was carried out with treating titania/cellulose-GPE with fuming sulfuric acid. The reaction was performed at room temperature for 20 h. The reaction mixture was poured into plenty of ice-water mixture and the precipitate was collected with a centrifuge. The collected product (titania/cellulose -SO_3H) was then dispersed in an acetic acid aqueous solution to result in a homogeneous solution for further application.

2.4. Synthesis of s-PBI polymer

1.28 g diaminobenzidine (6 mmol) and 2, 2-Bis(4-carboxyphenyl) hexafluoropropane (6 mmol) were mixed with PPA (38 g) and placed in a round-bottom flask equipped with a reflux condenser with an inlet for nitrogen. The mixture was heated to 190 °C for 20 h [32]. The polymerized PBI powder was collected and then dissolved in DMAc to