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Functionalization of track-etched poly (ethylene terephthalate) membranes as a selective filter for hydrogen purification

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ABSTRACT

This paper reports on the carboxylic and amino group functionalization of track-etched poly(ethylene terephthalate) (PET) membranes with different pore size and pore density. Glycolic acid groups were formed by oxidation of hydroxyethyl end groups while amino groups were introduced by amidation of these carboxylic groups with tetraethylenepentamine. These membranes were characterized by gel permeation chromatography (GPC), nuclear magnetic resonance (NMR) and X-ray photoelectron spectroscopy (XPS) to follow the effect of the oxidation process on the molecular weight of the PET and to access the formation of functional groups. As concluded from NMR and XPS results, the density of carboxyl and amino group increases in comparison to pristine PET membranes. The larger the pore diameter and the pore density, the higher is the extent of functionalization. We demonstrate the deposition of palladium (Pd) nanoparticles onto pore walls and pore surfaces of PET membranes for potential use in hydrogen separation or sensing. Scanning electron microscopy (SEM), transmission electron microscopy (TEM), and energy dispersive x-ray spectroscopy (in SEM) results show presence of Pd nanoparticles in functionalized PET membranes pointing to an enhanced binding capability of Pd nanoparticles that can be used for hydrogen extraction from a mixture of gases.

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Introduction

There is an increasing interest in developing new methods to functionalize the material surfaces for changing their surface properties according to required applications. The controlled functionalization of porous material is more

difficult in comparison to planar surface but it is more relevant for advanced functional materials such as membranes for mass separation. Poly (ethylene terephthalate) (PET) membranes are being used for various applications because of their excellent mechanical strength, inertness to many chemical reactions and resistance to thermal environment [1,2].

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Hydrogen is a very clean and promising energy source. Fuel cells are currently becoming one of the most promising solutions of energy and environmental problems and for this application pure hydrogen is required and its stable supply is important. Thus, there is demand for new materials and methods for hydrogen generation, storage, separation and sensing [3,4]. Palladium (Pd) and palladium alloys are regarded as the most important materials for high quality hydrogen extraction from a mixture of gases. Palladium-modified membranes have high hydrogen permeability, good chemical compatibility and excellent hydrogen selectivity [5–11]. Many efforts are being directed on the reduction of the membrane thickness in order to maximize hydrogen permeability and reduce the membrane cost [12–14]. In general, thinner and denser membranes show high performance for hydrogen permeation due to decreasing time through the membrane and increasing collision frequency between gas and wall of pores in membrane. However, the fabrication of an ultra-thin palladium-modified membrane is quite challenging and attracts innovative applications for separation technology and various devices [15,16]. An effort has been made by Yu et al. [1] by depositing Pd nanotubes within the pores of track-etched polycarbonate (PC) membranes by electroless plating method. Due to granular surface of nanotubes having high surface area they show high sensitivity and low detection limit for hydrogen sensing.

Functionalization of PET film with carboxylic group can be achieved by pulsed plasma deposition of maleic anhydride. This modified PET surface is useful for bioconjugation reaction [17,18]. The controlled pore functionalization of PET membranes with surface initiated atom transfer radical polymerization method has reported by Friebe et al. [16]. By this method they grafted functional polymer layer on PET pore walls. The grafted glycopolymer layer is useful for selective adhesion of bacteria and lectin binding [19,20]. Kuwahara et al. [21] investigated the immobilization of functional Au/CdS nanoparticles onto PET using supercritical CO₂. However, this method requires certain controlled environment and pressure for immobilization of nanoparticles in polymer. An alternative approach is the functionalization of polymer surface as well as pore walls by carboxylation and amination, where nanoparticles can be deposited as per required applications. In particular, different track-etched membranes of PC and PET have been widely used for selective binding of nanoparticles in pore walls. Whelove et al. reported carboxylation of PET mesh and its conjugation with 20 nm gold nanoparticles [22]. This PET/Au composite has improved biocompatibility in hernia repair materials. Functionalized calcium phosphate nanoparticles have deposited on track-etched PET membranes by Urch et al. [23]. They have observed that no particle absorption occurs on unmodified surface while functionalized surface binds the nanoparticles. Gas permeability and selectivity of track-etched membranes have investigated widely and found that permeability loses at higher selectivity or vice versa [24–30]. Acharya et al. has deposited Ti on track-etched polycarbonate membranes and found selectivity 4.72 for H₂ over CO₂ [25]. The functionalization of pore walls of track-etched membranes is an effective technique for depositing various

nanoparticles. These functionalized membranes offer advantages over the pristine or nanocomposite membranes, since different functionalities can be obtained and nanoparticles or nanotubes can be incorporated into the pore walls. The shape, size, charge and nature of nanoparticles can be tailored further for fabrication of functionalized membranes.

Deposition of a thin layer of Pd nanoparticles on pore walls of membrane after functionalization of membrane is a significant progress for a variety of applications. This work reports on the functionalization of track-etched PET membranes and on first results in the deposition of Pd nanoparticles on pore walls as well as surface of membrane by dip coating for potential use in hydrogen separation or sensing. The advantages of this technique are easy deposition over complex shapes, large area, simplicity and low cost. The results suggest that Pd nanoparticle deposited on PET membrane walls can play a device role in controlling the absorption. The schematic illustration of different membrane with different functional group is shown in Fig. 1.

Experimental

Materials

The track-etched PET membranes of higher pore density with pore sizes 0.1 μm and 0.2 μm were procured from it4ip s. a. (Seneffe, Belgium) and the track-etched PET membrane of 0.2 μm pore size with lower pore density was procured from Sterlitech Corporation (Kent, USA). The chemicals used for the functionalization of track-etched PET membranes were potassium permanganate (KMnO₄, Sigma Aldrich, Germany), palladium (II) chloride (99.999%, Sigma Aldrich, Germany), sulfuric acid (Merck, Germany), hydrochloric acid (Merck, Germany), N,N'-dicyclohexylcarbodiimide (Sigma Aldrich, Germany), N-hydroxybenzotriazole (Sigma Aldrich, Germany), sodium citrate (Sigma Aldrich, Germany), sodium borohydride (Sigma Aldrich, Germany), N,N-dimethylformamide (DMF, Sigma Aldrich, Germany), tetraethylenepentamine (Sigma Aldrich, Germany), and ethanol (VWR, Germany). They were used as received without any further purification.

Pd nanoparticle synthesis

Palladium (II) chloride was dissolved in concentrated hydrochloric acid in the molar ratio 1:2 and then diluted by deionized water to achieve the final metal precursor concentration of 10 mM. The precursor was filtered through hydrophilic syringe filter with 0.2 μm pore size. In a round bottom flask 88.5 ml deionized water was heated to 80 °C. Then 2.5 ml of the above filtered precursor was added, followed by the addition of 2 ml of 1% sodium citrate solution after 1 min. After 1 min 5.5 ml of freshly prepared 0.08% sodium borohydride solution in 1% sodium citrate was quickly injected and the system was left to react for 10 min. The brown solution was cooled to room temperature. Afterwards the resulting nanoparticle solution was filtered through hydrophilic syringe filter with 0.2 μm pore size.

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