

Decorating titanate nanotubes with protonated 1,2,4-triazole moieties for anhydrous proton conduction



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ABSTRACT

Anhydrous proton conducting materials based on surface attachment of protonated 1,2,4-triazole moieties on titanate nanotubes are prepared through self-assembly technique. ¹H MAS NMR spectra have revealed that the triazole moieties located at the outer surface of nanotubes. The distance between two ionic groups at the surface is observed to be shorter than 1 nm, which may facilitate the formation of continuous proton conducting domains, leading to easy proton transport through segmental motion and structural re-organization in the absence of water. The maximum proton conductivity of the synthesized materials reaches about $2.4 \times 10^{-3} \text{ S cm}^{-1}$ at 160 °C under anhydrous conditions.

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1. Introduction

Proton conducting materials have attracted considerable attention because of their promising applications as electrolytes for proton exchange membrane fuel cells (PEMFCs) [1,2]. The most commonly used and commercially available electrolyte material for PEMFCs is perfluorinated ionomer, known by its trade name Nafion, which composed of a poly(tetrafluoroethylene) backbone and fluorocarbon side chains terminated with sulfonic acid moieties. However, the humidity-dependent proton conductivity and relatively low glass transition temperature of Nafion limit its further applications in elevated temperature fuel cells [3–5]. Since PEMFCs operated at elevated temperature could benefit from enhanced tolerance to carbon monoxide and simplified heat management, it is worthwhile to seek new anhydrous proton conducting materials for elevated temperature fuel cell applications [6,7].

One important approach is to use low-volatile N-doped heterocycles including imidazole or triazole as proton conducting materials since they present high proton conductivity that is comparable to those of hydrated membranes, especially at operating temperature above 150 °C [8–14]. However, the employment of heterocycles as proton conductor for fuel cell membrane applications requires their immobilization to form membranes and to prevent their leakage from membranes during fuel cell operation. Attempts

towards immobilization of heterocycle moieties as proton conductors on polysiloxane matrix for anhydrous electrolytes have been developed [11–13]. However, the stability of the backbone and the according durability of such electrolytes during operation process may become a major issue for practical fuel cell applications. This has led our attention to immobilization of heterocycles onto inorganic matrix to form organic-inorganic hybrid electrolytes. Titanate nanotubes (TiNTs) were chosen as inorganic matrix in this study since the large amount of surface hydroxyl groups provide easy accessibility for surface modification and liquid-like surface induced by chemisorbed water molecules can facilitate proton transfer, particularly under reduced relative humidity [15,16].

Herein, we report the formation and proton transportation properties of a new type anhydrous proton conducting materials, where protonated 1,2,4-triazole moieties were chemically attached to the outer surface of TiNTs. It is hypothesized that the distance between two ionic moieties at the surface of TiNTs is quite short, which may facilitate proton transport through segmental motion and structural re-organization in the absence of water. The synthetic route of the proposed materials used in the present study were shown in Fig. 1.

2. Experimental

2.1. Formation of TiNTs

TiNTs were first synthesized according to literature [17]. Physical properties of the applied TiNTs were characterized to be

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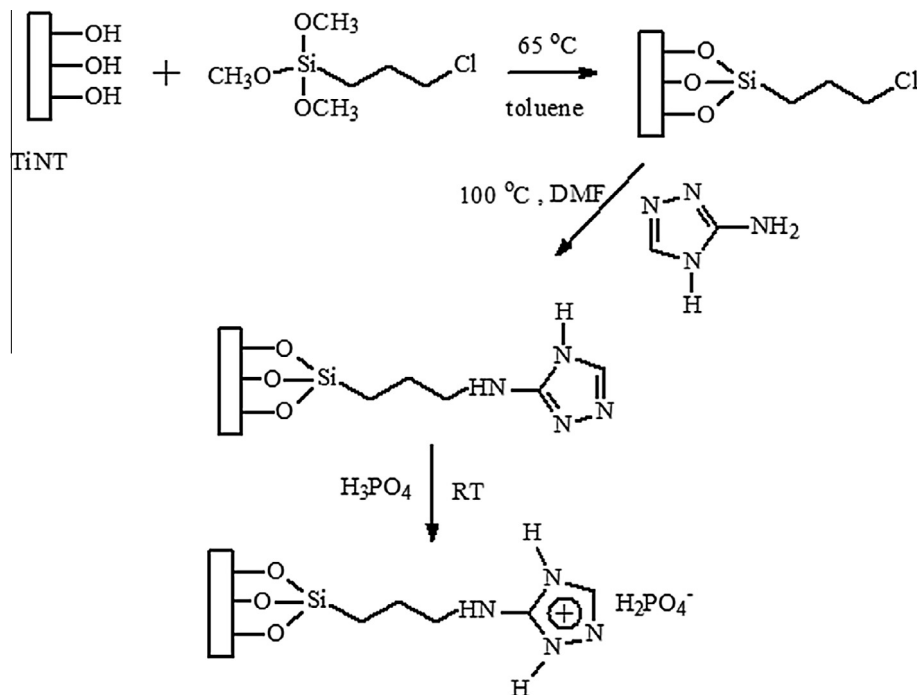


Fig. 1. Synthetic route of protonated triazole functionalized TiNT.

50–140 nm in length and 5 nm in inner diameter with the Brunauer–Emmett–Teller (BET) surface area of $321 \text{ m}^2 \text{ g}^{-1}$ calculated from adsorption–desorption isotherms, as shown in Fig. 2a. The SEM image of synthesized titanate nanotubes was displayed in Fig. 2b.

2.2. Synthesis of 1,2,4-triazole modified TiNTs

To a suspension of TiNTs (2 g) in anhydrous toluene (30 ml) at 65°C , a solution of 3-chloropropyltrimethoxysilane (4 g) in anhydrous toluene (20 ml) was added dropwise under an atmosphere of nitrogen. After stirred for 60 h, the mixture was centrifuged and washed with anhydrous toluene and anhydrous methanol several times until no un-reacted 3-chloropropyltrimethoxysilane was detected using thin layer chromatography. White powder (2.24 g) was obtained after vacuum dried at 60°C . The above synthesized white powder was re-dispersed in dry N,N' -dimethylformamide (DMF, 100 ml). After the suspension was heated to 100°C using an oil bath, a solution of 3-amino-1,2,4-triazole (0.42 g) in dry DMF (20 ml) was added dropwise under an atmosphere of nitrogen

and the mixture was stirred at 100°C for 40 h. The mixture was then centrifuged and the solid product was washed with dry DMF and methanol several times until no un-reacted 3-amino-1,2,4-triazole was detected using thin layer chromatography. After vacuum dried at 60°C , the final product (2.32 g) was obtained.

2.3. Formation of protonated 1,2,4-triazole modified TiNTs

1,2,4-Triazole modified TiNTs were immersed into H_3PO_4 aqueous solution (0.1 M, 500 ml). After stirred for 12 h at room temperature, the mixture was centrifuged and the solid product was extensively washed with deionized water several times until pH of 7.0 of eluent reached. The final product was vacuum dried at 60°C .

2.4. Characterization

X-ray photoelectron spectroscopy (XPS) measurements were performed on VG Multilab 2000 using monochromatic $\text{Mg K}\alpha$

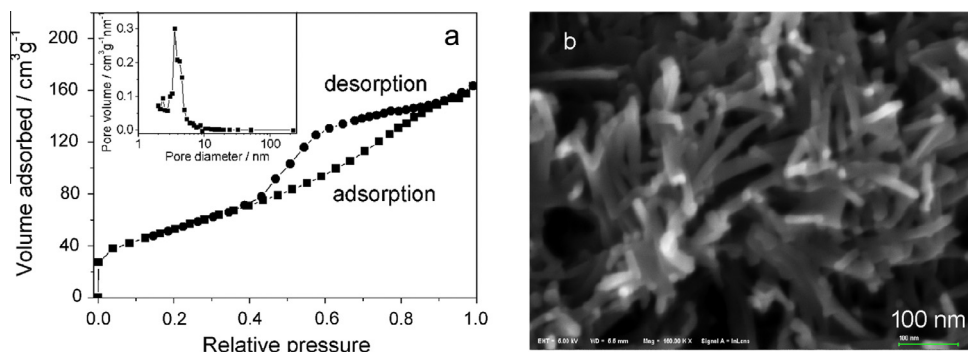


Fig. 2. (a) Pore volume and pore size distribution (inset) of the formed titanate nanotubes calculated from the adsorption–desorption isotherm, and (b) SEM image of formed titanate nanotubes.

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