



Fabrication of palladium–titania nanofiltration membranes via a colloidal sol–gel process



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ABSTRACT

Titania nanofiltration (NF) membranes with a molecular weight cut-off (MWCO) of ~ 1000 Da impregnated with noble metal Pd have been fabricated via the colloidal sol–gel route. The process of calcination under air atmosphere before reduction under hydrogen atmosphere was utilized for complete removal of organics, and the as-prepared Pd-doped TiO_2 materials were denoted as PdO– TiO_2 and Pd– TiO_2 , respectively. XRD patterns and TEM images confirmed that, under the air atmosphere, the Pd doping restrained TiO_2 grain growth and A \rightarrow R transformation, which may be due to the substitution of Pd^{2+} into the TiO_2 lattice, suggesting that the release of deformation energy stabilized the anatase phase. Combining N_2 adsorption–desorption results, the PdO– TiO_2 materials with a Pd concentration of 30 dwb% and a calcination temperature of 400 °C were optimized with a pore size of 1.7 nm. After hydrogen reduction, the inhibitory effect of Pd doping on phase transformation was weakened, with a looser pore structure achieved for the Pd– TiO_2 materials with a pore size of 2.4 nm, indicating the inhibitory effect of PdO, Pd^0 and Pd^{2+} , the three chemical states of elemental Pd, on TiO_2 crystal growth and A \rightarrow R transformation improved in turn. Finally, the Pd– TiO_2 NF membranes were fabricated with a water permeability of ~ 10 L/(m^2 h bar), showing high ion retention rates, while the undoped TiO_2 membranes exhibited much lower retention properties.

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1. Introduction

Nanofiltration (NF) is a unit process that has undergone recent rapid development. The process is used to separate mixtures at the molecular level. Nanofiltration has been studied in great detail and applied to many fields, including food, pharmaceutical and water purification. NF membranes are commonly used for the retention of solutes with a molecular weight of 200–1000 Da, small ionic components or inorganic salts. Ceramic NF membranes, compared to organic polymeric NF membranes, are expected to perform more reliably in industrial applications due to their high resistance to harsh environments [1–3]. Therefore, a great deal of research has been focused on the development of ceramic NF membranes.

The sol–gel process has been considered to be the main technique for the fabrication of ceramic NF membranes, during which the polymeric route was the most frequently used. To date, many different types of materials have been made via this route, including γ - Al_2O_3 [4–6], TiO_2 [7–11], ZrO_2 [12–15] and TiO_2 - ZrO_2 [16]. For production on an industrial scale, the colloidal route will be preferred due to its characteristics of easy operation and low

volatilization. To the best of our knowledge, only a few materials, such as HfO_2 [17–19] and SiO_2 - TiO_2 [20–22], have been fabricated via this route. A difficulty related to the fabrication of ceramic NF membranes via the colloidal sol–gel technique may be the synthesis of materials with individual grains less than 10 nm throughout the process, based on particle packing models of random closed-packed systems [23,24].

For TiO_2 materials, owing to their excellent thermal and chemical stability, much attention has been focused on the development of nanosized TiO_2 materials. In spite of that stable TiO_2 particulate sol with particle size below 10 nm has been synthesized during the past years [25–27], it should be more crucial to preserve the individual grains of less than 10 nm throughout the thermal process in order to achieve a suitable TiO_2 material for NF membrane formation. On the other hand, for TiO_2 materials, the phase transformation from anatase (A) to rutile (R) will introduce a volume change of approximately 8% [28], which should be strictly avoided because it would induce film cracking in the formed membranes.

Consequently, the inhibition of grain growth has been considered important for maintaining the pore size of TiO_2 materials in the range of 1–2 nm and restraining the A \rightarrow R transformation. In the past few decades, progress has been made in inhibiting the

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A → R transformation, either by changing the chemistry of the sol–gel system or by varying the drying and sintering process [29,30]. Over the years, more efforts have been made to dope TiO₂ with metallic [31,32] or non-metallic [33,34] elements to develop new photocatalysts, among which the metallic doping is also reported to influence the A → R transformation. In the literature, several metal elements were reported to retard the A → R transformation, such as Zr, Fe, Mg and Pd. Actually, the doped metal element often exists as metallic oxide, such as ZrO₂, which is still chemically stable, while Fe₂O₃, MgO or PdO will react with acid and reduce the chemical stability of TiO₂ in acidic environment.

In the present paper, we fabricated TiO₂ NF membranes by doping palladium (Pd) metal, which is chemically inert and the most commonly used precious metal element [35–37], via the colloidal sol–gel process for nanofiltration. Considering the very thin membrane thickness involved, generally less than 1 μm, the increased expense induced by Pd can be neglected. The process of calcination under oxygen atmosphere before reduction under hydrogen atmosphere has been accepted for the complete removal of organics, and the as-prepared Pd-doped TiO₂ materials were denoted as PdO–TiO₂ and Pd–TiO₂, respectively. Ahmad et al. [38] reported the synthesis of Pd–TiO₂ UF membranes with a pore size of 10 nm for hydrogen separation. The membranes were fabricated by reducing PdO–TiO₂ membranes under H₂ atmosphere, and the emphasis was given to the influence of Pd doping on microstructure of the reduced Pd–TiO₂ materials. In our work, the effects of Pd doping on the microstructure of the unreduced PdO–TiO₂ materials were detailedly studied via X-ray diffraction (XRD), N₂ adsorption–desorption analysis, transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). Then, the effect of the different chemical states of elemental Pd on the microstructure of TiO₂ materials was also investigated. Finally, the performance of the as-prepared Pd–TiO₂ membranes and the undoped TiO₂ membranes was determined by measuring the pure water flux, the MWCO and the retention properties with respect to electrolyte solutions, such as MgCl₂, LiCl, Na₂SO₄ and NaCl.

2. Experimental

2.1. Materials

Titanium (IV) isopropoxide (TTIP, Sigma–Aldrich, 97%), isopropanol (IPA, Aldrich, ≥99.7%), diethanolamine (DEA, Sigma–Aldrich, 99%), nitric acid (HNO₃, Sigma–Aldrich, 70%) and a palladium (II) nitrate solution (Johnson Matthey catalyst Co., Ltd., 15.199 wt%) were used as received for the synthesis of nanosized TiO₂ and Pd-doped TiO₂ particulate sols.

Asymmetric α-Al₂O₃ tubular microfiltration membranes (pore diameter of 0.2 μm) with an inner diameter of 8 mm and an outer diameter of 12 mm were supplied by Jiangsu Jiuwu Hi-Tech, on the inner surface of which boehmite (γ-AlOOH) precursor sol (~30 nm) were coated and sintered to fabricate γ-Al₂O₃ ultrafiltration interlayers (with a MWCO of 6000 Da) for subsequent NF top layer formation.

2.2. Preparation of TiO₂, Pd-doped TiO₂ colloidal sols and materials

A titania colloidal sol was prepared as follows. A specified amount of TTIP, which was partially complexed by DEA, was dissolved into IPA for 60 min. Then, the homodispersed solution was added dropwise to excess water at 45 °C for 1 h with vigorous stirring for complete hydrolysis of TTIP. Then, the stirring was maintained for 6 h after HNO₃ was added to the precipitate for peptization, and a transparent sol was formed. The molar ratio of TTIP: DEA: HNO₃:H₂O was 1:0.8:2.4:1000.

Pd-doped TiO₂ colloidal sols with different amounts of Pd-doping were prepared using a similar procedure, except for specific amounts of palladium (II) nitrate solution were added at the onset of TTIP hydrolysis.

A TiO₂ material was synthesized by pouring the titania colloidal sol into a Petri dish, followed by dried in humid air at 60 °C for 4 h and calcinated at 350–500 °C with the heating and cooling rate of 0.5 °C/min. A PdO–TiO₂ material was fabricated with the Pd-doped TiO₂ colloidal sol by the same process as the TiO₂ material. A Pd–TiO₂ material was prepared by reducing the PdO–TiO₂ material under hydrogen at 300 °C for 2 h.

For quick reference, each material was numbered based on its Pd content, which included 0, 25, 30, 35 and 40 dwb% (on a dry weight of TiO₂ basis, dwb), with the molar ratio of Pd/Ti of 0, 0.25, 0.32, 0.41 and 0.50, respectively, as listed in Table 1.

2.3. Preparation of supported PdO–TiO₂, Pd–TiO₂ and undoped TiO₂ membranes

A supported PdO–TiO₂ membrane was formed by dip-coating the inner surface of a γ-Al₂O₃ UF membrane with a freshly prepared sol solution for 6 min, followed by dried in humid air at 60 °C for 4 h. Then repeat the dip-coating, drying process once before the membrane was calcinated at 400 °C with the heating and cooling rate of 0.5 °C/min. A supported Pd–TiO₂ membrane was formed by reducing the PdO–TiO₂ supported membrane under hydrogen at 300 °C for 2 h. An undoped TiO₂ membrane was prepared with the TiO₂ colloidal sol by the same process with the PdO–TiO₂ membrane.

2.4. Characterization

For XRD, TEM, XPS and N₂ adsorption–desorption analysis, the materials were ground to form a fine-powdered sample. The crystal structure and phase composition were investigated by powder X-ray diffraction (Rigaku SmartLab X-ray diffractometer) at 45 kV and 200 mA using Cu Kα radiation (λ = 0.154 nm) with 2θ ranging from 20° to 80°. The crystallite size was estimated from the Scherrer's equation using the FWHM of the (101) peak of anatase. The BET specific surface area, pore size distribution and pore volume of the sample were characterized by N₂ adsorption–desorption (BELSORP Mini) at a temperature of 77 K. TEM (JEOL JEM-2100 transmission electron microscope) was performed to confirm the crystallite size of the sample, which was sonicated and then dispersed on a TEM carbon grid. The chemical state and composition were determined by XPS (VG ESCALAB MK II spectrometer, Al Kα 1486.6 eV photons).

The water permeability of the supported membranes was determined using a tangential-flow apparatus by measuring the flux rate of deionized water under pressures ranging from 0.4 MPa to 0.8 MPa. The MWCO of the membranes was evaluated by measuring polyethylene glycols (PEG, Sigma–Aldrich, >99%) retention at a pressure of 0.5 MPa and a temperature of 293 K. PEG retention was determined using an aqueous solution containing PEG of different molecular weights. Two types of solutions were involved, which

Table 1
Code of samples for TiO₂ materials with different amounts of Pd doping.

Code of samples	Pd mass fraction (dwb% TiO ₂)
Pd-0-TiO ₂	0
Pd-25-TiO ₂	25
Pd-30-TiO ₂	30
Pd-35-TiO ₂	35
Pd-40-TiO ₂	40

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