Solvent free fabrication of nanoporous TiO₂ filters using organic–inorganic nanocomposites

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ABS TRACT

Nanoporous TiO₂ filters with 50 nm mean pore size are synthesized by using commercial TiO₂ nanoparticles and polyvinylpyrrolidone with an easy and low cost route that did not involve any solvent. Crystal structure and surface morphologies are studied by X-ray diffraction (XRD) and scanning electron microscopy (SEM), respectively. X-ray photoelectron microscopy (XPS) is used to confirm the filtering process by analyzing pre- and post-filter affluent containing nanoparticles to simulate the filtration of micrometer (bacteria) and nanometer (virus) species. Greater than 85% filtering efficiency is obtained during the filtering of a mixture of water and 30 nm mean crystallite size iron oxide nanoparticles.

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1. Introduction

It is estimated that 88% of the deaths caused by gastronomical diseases are due to the use of unsafe water [1]. Globally, more than 2.6 billion people have no access to proper sanitation facilities [1]. In the age of technology these numbers are unacceptably high and need very serious attention.

There are several water purification methods that are in current practice. Most general methods of boiling and pasteurization [2], and reverse osmosis, which is used by most of the water companies, are not good choices because both of these methods require large amount of energy. Chlorination is also a practical choice but it is hard to use for small areas and at the point-of-use. UV treatment is frequently used but this method presupposes the existence of electricity for the generation of UV.

It is for these reasons that ceramic nanoporous water purifiers are of interest. These filters have the potential of being low cost solutions for point-of-use water purification to reduce diarrheal diseases [3]. There has been much work done on ceramic filters but the general configuration of these filters includes a microporous filter with a nanoporous coating [4] which sometimes can also act as a photocatalytic layer [5]. Photocatalytic layers are generally used for giving a self-cleaning property to the filters to oxidize organic materials by exposing the filters to light which increases the usage time and reduces the cost.

Some metals show antibacterial and photocatalytic activities, particularly when they are in the nanoparticle form. The best example of antibacterial metal is silver [4,6]. However, the application of these metals is limited by cost. Most of the time the economical solution is to use them as coatings or particle dispersion. Coatings or particles can be deposited chemically or through the use of more sophisticated techniques that raises the cost of product [4,7].

TiO₂ nanoparticle filters are also good photocatalytic materials and are commonly used as a coating material for ceramic filters [8]. TiO₂ nanoparticles are relatively cheap, stable and biocompatible but, just as the other coating materials, require special coating techniques to coat the ceramic filter. This additive process increases the cost and reduces the lifetime time because of the poor adhesion between the ceramic filter and the TiO₂ particles. In addition to being used as coating, TiO₂ can also be used as a bulk ceramic membrane filter. There are few reported methods for making TiO₂ bulk membrane filters in the literature [9,10]. One of the most used methods involves mixing polymer solutions with TiO₂ nanoparticles to make a composite structure followed by heat treatment to burn the polymer and obtain a porous structure [9]. However, this method does incur substantial cost and the risk of environmental hazards also increases because of the usage of the solvents. There are other methods described in the literature that utilize templates, e.g., conductive wires [11] or biotemplates [12].

In this paper we describe an easy and inexpensive technique to make a nanoporous TiO₂ filter directly from commercial TiO₂ nanoparticles and polyvinylpyrrolidone without using any solvents. The fabricated filter is tested for the filtering efficiency by using iron oxide nanoparticles to
simulate micrometer (bacteria) and nanometer (virus) species that might be present in the water. The use of iron oxide nanoparticles as a simulator for bacteria and viruses is unconventional. However, our only intention in using these nanoparticles is to demonstrate the size selectivity of the filters. Indeed it is possible that there be an interaction between iron oxide and TiO₂ and between the bacteria and viruses but in either case of our efficiency results we will be erring on the positive side, i.e., both these interactions will promote the filtering efficiency.

2. Material and methods

TiO₂ nanoparticles (Degussa P25) with average particle size of 21 nm and polyvinylpyrrolidone (Sigma-Aldrich PVP10) are used as starting materials. The starting material is a mixture of PVP10 and P25 TiO₂ with a ratio of 1:4 (PVP10:TiO₂) which is heated up to 170 °C on a hotplate in a Pyrex beaker and stirred with a magnetic stirrer for 30 min while keeping the temperature constant. This mixture is used as the precursor for the filters. 70 mg of the precursor is pressed into 12 mm diameter and 0.5 mm thick disks with an open-bottom die on an alumina substrate which helps in manipulating the filter easily.

The pressed disks are calcined on a hot plate in an ambient atmosphere up to a temperature of 550 °C in several steps to burn the PVP. First, the disk is heated to 175 °C for 20 min. The temperature is then raised to 300 °C and the disks are heated at this temperature for 20 min. The temperature was further increased to 400 °C and eventually to 500 °C and 550 °C and the disks are kept at each of these temperatures for 15 min. Stepwise heating allowed slow removal of PVP10 without any explosive evolution of the byproducts or excessive shrinkage and to maintain the physical integrity of the filter. The disks were then allowed to cool down in 15 min. The calcined samples are placed in a furnace on an alumina plate for sintering. Sintering is carried out at 600 °C. Temperature was raised to 300 °C and the disks are heated at this temperature for 20 min. The temperature was then increased to 500 °C and 550 °C and the disks are kept at each of these temperatures for 15 min. Stepwise heating allowed slow removal of PVP10 without any explosive evolution of the byproducts or excessive shrinkage and to maintain the physical integrity of the filter. After sintering samples were taken out and air-quenched to room temperature to stop any further crystal growth.

The crystalline structure analyses of the precursor, calcined, and sintered samples are carried out in a Rigaku D-max B X-ray diffractometer using Cu Kα radiations (Table 1). Crystal structure parameters are calculated by using the Rietveld software MAUD 2.33 from X-ray powder diffractions patterns [13]. A Jeol JSM-7400 F SEM was used to study the surface morphology of the samples. Filtration properties of the samples were evaluated indirectly by using nanometer size Fe₂O₃ particles as a simulator for the bacteria and some viruses. Fe₂O₃ is insoluble in water of pH = 7 [14]. Fe₂O₃ nanoparticles (Nanophase NanoTek Iron Oxide ~30 nm) were dispersed in distilled water in a 3/10 mass ratio by using an ultrasonic homogenizer for 1 min. This mixture was immediately used as the “unfiltered” water. The schematic of the filtering system is shown in Fig. 1. The sintered disk filters were placed in the opening of a small aluminum case and the edges were sealed with glue. The unfiltered water–Fe₂O₃ mixture was forced in to the Al case and the filter using a syringe. The “filtered” water is collected on the other side of the filter.

Both filtered and unfiltered water samples are analyzed for iron using an Omicron (Al Kα) X-ray photoelectron spectrometer (XPS). For XPS analyses few drops of filtered and nonfiltered Fe₂O₃ water mixtures are placed on two separate XPS sample holders and allowed to dry at room temperature. These samples were then inserted in the XPS chamber. XPS data are recorded in survey and high resolution formats using pass energies of 50 and 25 eV, respectively. XPS data is analyzed using C 1s (284.5 eV) and Iron 2p (710 eV) peaks. As a reference, pure distilled water is passed through the filtering system and XPS samples were prepared and analyzed following the same procedure as described above.

3. Results and discussion

The results of the XRD analyses are shown in Fig. 2. The XRD pattern of the precursor powder shows a mixture of 90% anatase and 10% rutile phases with crystallite sizes of 34 nm and 74 nm for anatase and rutile particles, respectively, as calculated by the Scherer’s formula. The bulk transformation temperature from rutile to anatase is around 550 °C. However, this transformation temperature becomes much lower for thin films and nanoparticles [15,16]. Therefore, it is expected that sintering, which was done at 550 °C, will cause the rutile phase to transform to anatase phase. However, samples sintered at 550 °C were very fragile due to poor bonding between the particles. SEM images in Fig. 3a and b show this poorly bonded structure suggesting that these TiO₂ structures need higher temperatures for sintering. TiO₂ crystal structure can be refined very fast at temperatures of 600 °C or above.

### Table 1

Results of Rietveld analysis of the XRD patterns.

<table>
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<tr>
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<th>Precursor</th>
<th>Calcined</th>
<th>Sintered</th>
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<tbody>
<tr>
<td>Anatase (%)</td>
<td>90.0 ± 1.0</td>
<td>72.9 ± 1.4</td>
<td>20.7 ± 1.0</td>
</tr>
<tr>
<td>Rutile (%)</td>
<td>9.7 ± 0.5</td>
<td>27.0 ± 0.9</td>
<td>79.2 ± 2.0</td>
</tr>
<tr>
<td>Anatase (Å)</td>
<td>3.7909 ± 0.0006</td>
<td>3.7828 ± 0.0006</td>
<td>3.7819 ± 0.0009</td>
</tr>
<tr>
<td>c (Å)</td>
<td>9.5203 ± 0.0009</td>
<td>9.5069 ± 0.0009</td>
<td>9.5146 ± 0.0009</td>
</tr>
<tr>
<td>Crystallite size (Å)</td>
<td>348 ± 7</td>
<td>379 ± 11</td>
<td>1102 ± 47</td>
</tr>
<tr>
<td>Rutile (Å)</td>
<td>4.6035 ± 0.0001</td>
<td>4.5914 ± 0.0008</td>
<td>4.5912 ± 0.0005</td>
</tr>
<tr>
<td>c (Å)</td>
<td>2.962 ± 0.0011</td>
<td>2.9576 ± 0.0006</td>
<td>2.9585 ± 0.0003</td>
</tr>
<tr>
<td>Crystallite size (Å)</td>
<td>721 ± 14</td>
<td>759 ± 29</td>
<td>1102 ± 47</td>
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Fig. 1. Schematic of the filtering system.
Fast crystal growth is considered a good property for ceramic structures because the structure can then be made durable and smooth. However, for a filter, it is an undesirable property as fast crystal growth can close the pores quickly, restrict water flow and decrease the filter performance. Nevertheless, it is possible to accurately control the sintering such that crystal growth can be limited. Quenching can also help control the pore size. In our case the optimum time and temperature measured for the best filter performance included sintering at 600 °C for 5 min immediately followed by air quenching. After sintering the structure became mechanically durable while still maintaining the desired porosity, as can be seen from the SEM images in Fig. 3c and d. The mean pore size determined from SEM images is 50 nm. BET analyses yielded the post-annealing surface area to be $42 \pm 5 \text{ m}^2/\text{g}$, pore volume $0.1 \pm 0.02 \text{ cm}^3/\text{g}$, and the pore size $27 \pm 3 \text{ nm}$. The discrepancy between the SEM and BET results is most probably due to the interpretation of the two dimensional SEM micrographs for a 3-D quantity and, as such, the BET results are more reliable.

According to X-ray powder diffraction analyses, the mean crystallite size becomes larger than 100 nm, as also supported by SEM. The grain growth and sintering suggest strong interparticle bonds and a good crystal structure. Additionally, because of the sintering at 600 °C, approximately 79.2% of sample became rutile. As mentioned above, filter performance was evaluated indirectly by determining the filtering efficiency for the Fe$_2$O$_3$ nanoparticles using XPS. To calculate the change in the amount of the Fe$_2$O$_3$ nanoparticles in the water before and after filtering, iron 2p$_{1/2}$ and 2p$_{3/2}$ peaks are normalized by dividing their areas to carbon 1 s peak area to avoid the differences between the measurements (Fig. 4). Areas under 2p$_{1/2}$ and 2p$_{3/2}$ peaks are calculated by integrating the peak intensities. Results are presented in Table 2. Since a non monochromatic, unfocussed X-ray source was used, in order to measure the correct integrated intensity of iron (oxide) that is coming from sample, the sample holder integrated peak intensity was subtracted from the filtered and unfiltered samples. For the filtered water Fe 2p peaks are barely above the Fe 2p signal intensity of the pure water signal. The corrected areas show that 82% of the Fe$_2$O$_3$ nanoparticles were separated by the filter.

The use of Fe$_2$O$_3$ nanoparticles as a simulant for bacteria and viruses is unique. Our intent is to demonstrate the filtration efficiency simply on the basis of size selection. It must be emphasized that although Fe is more electronegative (1.83 Pauling units) than Fe (1.54 Pauling units), and it is possible that a reduction of Fe$_2$O$_3$ could take place with a simultaneous change in its particle size as a result of

Fig. 2. X-ray powder diffraction pattern of precursor powder (a) calcined up to 550 °C and (b) sintered at 600 °C for 5 min.

Fig. 3. SEM micrographs of calcined (a, b) and sintered (c, d) samples.
this reduction, and no such reduction or particle size change were observed by SEM or by XPS analyses. Therefore, we believe that using Fe₂O₃ as a simulant just for the size selectivity is permissible.

4. Conclusion

TiO₂ nanoporous filters have a big potential for self cleaning and point-of-use water filtering to provide cheap and easy filtering in rural areas to reduce the gastronomical diseases. For this purpose nanoporous TiO₂ filters which have a 50 nm pore size are made by using TiO₂ nanoparticles and PVP10 which are both biocompatible and non-hazardous materials with an easy and low cost method that does not contain any solvent. Using Fe₂O₃ nanoparticles, the filtering performance of the filter was evaluated to be 82%.

Acknowledgment

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Table 2

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<tr>
<th></th>
<th>Total peak area</th>
<th>Corrected area</th>
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<tbody>
<tr>
<td>Empty holder</td>
<td>0.348</td>
<td></td>
</tr>
<tr>
<td>Filtered water</td>
<td>0.499</td>
<td>0.151</td>
</tr>
<tr>
<td>Non-filtered water</td>
<td>1.195</td>
<td>0.847</td>
</tr>
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</table>

Fig. 4. Normalized Fe peaks (2p 3/2 and 2p 1/2) of nonfiltered water, filtered water and sample holder.

References