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## Abstract

Poly(butyl methacrylate) (PBMA) colloidal crystal templates were assembled orderly on the clean substrates of monocrystalline silicon by dip-drawing technique and titanium dioxide (TiO2) macroporous membranes were prepared by using sol-dipping template method to fill the interstices among the PBMA templates, followed by calcination to remove the templates at 550℃. Calcination of the PBMA templates was carried out according to the following procedure: the rate of rising temperature was 5℃/min from room temperature to 150℃, 2℃/min from 150℃ to 270℃, 1℃ /min from 270℃ to 430℃, 2℃/min from 430℃ to 550℃ and maintained it at 550℃ for 2h. X-ray diffraction (XRD) spectra indicated the macroporous materials were anatase structure. The polymerization mechanism of BMA with Fenton reagent as a new initiator was discussed, and the removal process of the PBMA templates and the formation of TiO2 pore size were investigated, respectively. The results showed that the new method of polymerization overcomes many problems associated with the conventional emulsion polymerization techniques such as long reaction time, necessary deoxygenation, and complicated operation.



## Keywords

colloid, pbma, membrane, macroporous, tio2, ordered, preparation, template, crystal


## Disciplines

Life Sciences | Physical Sciences and Mathematics | Social and Behavioral Sciences


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# Preparation of ordered $TiO_2$ macroporous membrane using PBMA colloid crystal as template

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**Key Words:** Poly(butyl methacrylate) microspheres, Fenton reagent, $TiO_2$ macroporous membrane, sol-gel method, dip-drawing

**Abstract:** Poly(butyl methacrylate) (PBMA) colloidal crystal templates were assembled orderly on the clean substrates of monocrystalline silicon by dip-drawing technique and titanium dioxide ($TiO_2$) macroporous membranes were prepared by using sol-dipping template method to fill the interstices among the PBMA templates, followed by calcination to remove the templates at 550℃. Calcination of the PBMA templates was carried out according to the following procedure: the rate of rising temperature was 5℃/min from room temperature to 150℃, 2℃/min from 150℃ to 270℃, 1℃ /min from 270℃ to 430℃, 2℃/min from 430℃ to 550℃ and maintained it at 550℃ for 2h. X-ray diffraction (XRD) spectra indicated the macroporous materials were anatase structure. The polymerization mechanism of BMA with Fenton reagent as a new initiator was discussed, and the removal process of the PBMA templates and the formation of $TiO_2$ pore size were investigated, respectively. The results showed that the new method of polymerization overcomes many problems associated with the conventional emulsion polymerization techniques such as long reaction time, necessary deoxygenation, and complicated operation.

## Introduction

With the development of industries in the past decades, water pollution has been becoming a more and more serious problem in China. Furthermore, China is one of the countries which are encountering many difficulties with water scarcity. Undoubtedly, advanced treatment for wastewater and water reuse are the valid measures to resolve the problems as stated above. Membrane separation technique therefore is playing an important role in wastewater treatment and water reuse due to its efficient without requiring a phase change, continuous operation and little chemical addition required. However, a major obstacle to futher use in water treatment is flux decline resulting from fouling[1]. Several strategies to reduce fouling have therefore been investigated in recent years including the use of $TiO_2$ membrane coupled with photocatalytic effects [2-4].

$TiO_2$ has been intensively investigated as a semiconductor photocatalyst since Fujishma and Honda discovered the photocatalytic splitting of water on $TiO_2$ electrodes in 1972[5]. Recently, $TiO_2$ macroporous membrane material has mainly been the focus of numerous investigations because of its high hydrophilicity, stable chemical property, innocuity and low cost, etc[6]. Due to the macroporous materials with large pore, uniform distribution and ordered distribution[7], respectively, these materials have potential applications in many fields such as photocatalysis[8], filtration[9], solar cell material[10] and so on.

Up to now, the template technique showing simply and rapid processes with colloidal crystals could be the main methods for preparing the ordered macroporous materials. The result shows not only narrow distribution of macroporous materials pore size but also high of void fraction[11].

This is the first report on the preparation of the macroporous materials using template method with PBMA colloidial crystals. In the present work, the PBMA microspheres templates are synthesized by soap-free emulsion polymerization using Fenton reagent as a new initiator. Comparing with traditional technology[12], this technique has some advantages such as simple operation, quick polymerization, and without deoxygenation in all reaction process. The $TiO_2$ precursor solution is then filled in the gaps of the PBMA template by using sol-dipping method, followed by calcination to remove the templates. Thus, the ordered $TiO_2$ macroporous membranes are obtained.

**Materials and methods**

2.1 Materials

In the preparation of PBMA colloidal crystal template and $TiO_2$ sol, the following materials were used: butyl methacrylate (BMA, CP, distillated before experiment) and polyvinylpyrrolidone (PVP, K-30) was purchased from Sinopharm Chemical Reagent Co. Ltd, ferrous sulphate ($FeSO_4$, GR), hydrogen Peroxide ($H_2O_2$, 30%), hydrochloric acid (HCl, AR) and ammonia ($NH_3 \cdot H_2O$, 25% ) was obtained from Tianjin Kermel Chemical Reagent Co. Ltd), tetrabutyl titanate (TBOT, CP, purchased from Shanghai SSS Reagent Co. Ltd), triethanolamine (TEA, AR, purchased from Tianjin FuYu Fine Chemicals Co. Ltd), polyethylene glycol (PEG4000, purchased from PaiNi Chemical Reagent Company), absolute ethyl alcohol (EtOH, AR, purchased from Tianjin Fengchuan Chemical Reagent Science and technology Co. Ltd).

2.2 Experiment

2.2.1 Synthesis of monodispersed PBMA microspheres

Non-crosslinked, monodispersed PBMA microspheres were synthesized by using a soap-free emulsion polymerization technique. BMA purified for wiping off the inhibitor was added in the solution mixed with 0.12g of PVP, 30mL of $H_2O$ and 10mL of EtOH, followed by the addition of HCl to adjust pH 3.0~4 .0. Then, Fenton reagent used as a novel initiator, i.e. 0.005g of $FeSO_4$ and 100μL of $H_2O_2$, was added in the mixed solution. After complete addition the mixed solution was stirred for 8 h at 70℃ with stirring speed of 300 rpm. The resulting emulsion spheres were remained suspended in the mother liquor until needed.

2.2.2 Assembly of the PBMA colloidal crystal templates.

The PBMA colloidal crystal templates were assembled on the substrates of monocrystalline silicon piece by the dip-drawing technique. Firstly, the substrates (1cm×3cm) were cleaned ultrasonically for 30 min in the solution mixed with $H_2O_2$ (30%), $NH_3 \cdot H_2O$ and deionized water with a certain proportion of 1:1:2. Then, the clean and dried substrate was immersed vertically in the emulsion of PBMA for 5min. Finally, the substrate was slowly drew out (drawing speed of 0.1cm/min) and dried at 30℃ for 15 min. After the procedure was performed as mentioned above, an opalescent PBMA template with prismatic colors like rainbow was resulted, depending on the angle of observation.

2.2.3 Synthesis of $TiO_2$ sol

$TiO_2$ precursor solution was prepared by sol-gel method at room temperature according to the following procedure: TBOT was dissolved in the mixture solution of 35mL EtOH and 2.5mL TEA under vigorous stirring and kept for 2 h (solution A). Then solution B (0.5mL of deionized water and 5mL of EtOH) was dropped into solution A, followed by the addition of 0.1g of PEG (4000) under vigorous stirring and kept for another 2h at room temperature. Thus, the homogeneous, transparent and stabilized of $TiO_2$ sol with yellowish green color was obtained.

2.2.4 Preparation of $TiO_2$ macroporous membrane

Sol-dipping template method was used to fill $TiO_2$ sol into the interstices among the PBMA templates. Firstly, the substrate of monocrystalline silicon with PBMA array template on it was immersed in $TiO_2$ sol and kept for 1 min. Then the substrate was drawn out from sol and dried at room temperature for 3h to form a solid structure around the microspheres, followed by calcination to remove the PBMA template as the following recipe: calcination of the macroporous membrane was carried out in air with a heating rate of 5℃/min from room temperature to 150℃, 2℃/min from 150℃ to 270℃, 1℃/min from 270℃ to 430℃, 2℃/min from 430℃ to 550℃ and maintained it at 550℃ for 2h, respectively.

2.3 Characterization

The diameter of the PBMA microspheres was estimated using transmission electron microscopy (TEM, JSM-2001). Morphologies of the templates and macroporous membrane were examined using field emission scanning electron microscope (FESEM, JSM-7001F). X-ray diffraction (XRD) patterns of $TiO_2$ thin films were recorded on a Bruker $D_8$ Advance X-ray diffractometer operated at 40kV and 35mA using Cu Kα radiation and nickel filter (λ=0.15406 nm). The thermal-decomposition behavior of the PBMA template filled with $TiO_2$ precursor was monitored using a DTA/TG instrument (Diamond, USA).

## Result and discussion

3.1 Reaction mechanism

3.1.1 Reaction mechanism of Fenton reagent

Fenton reagent is a redox initiation system consisting of $Fe^{2+}$ and $H_2O_2$. The chain reaction between $Fe^{2+}$ and $H_2O_2$ in acidic medium can catalyze ·OH free radical which the oxidation potential is 2.8V. The reaction process [13] is as follows:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + \cdot OH \quad (1)$$

$$Fe^{2+} + \cdot OH \rightarrow Fe^{3+} + OH^- \quad (2)$$

$$H_2O_2 + \cdot OH \rightarrow H_2O + \cdot OOH \quad (3)$$

$$Fe^{2+} + \cdot OOH \rightarrow Fe^{3+} + OOH^- \quad (4)$$

$$Fe^{3+} + \cdot OOH \rightarrow Fe^{2+} + H^+ + O_2 \quad (5)$$

3.1.2 Reaction mechanism of PBMA microspheres

The homogeneous system in this work is composed of monomers, initiator, stabilizing agent and dispersion medium. When a given temperature is reached, the polymerization of -C=C- double bond in BMA could be carried out by ·OH caused by Fenton reagent. As expected, increased molecular weight decreased the solubility of polymer, and once the chain length is increased to a critical value, the polymer should be separated and precipitated from the dispersion medium. Then, the primary nuclear shells of polymer are generated by stabilizing agent and held in suspension solution. Consequently, the volume of nuclear shell is increased with the ongoing polymerization because there are also monomers and free radical in the primary nuclear shell. Therefore, the microspheres of PBMA will be formed.

3.2 Preparation of PBMA microspheres

To clarify the reaction mechanism of PBMA microspheres, we also investigated the influence of BMA monomer content, initiator content and reaction temperature on PBMA polymerization, respectively. Generally, with increasing amount of BMA monomer and reaction temperature, PBMA microspheres of large size are formed. However, smaller size of microspheres can be obtained if we increase the weight ratio of initiator content. Figure 1 shows the TEM image of PBMA microspheres prepared in this work. It can be seen that the average diameter size of PBMA microspheres is about 500 nm and the size deviation is less than 10%.

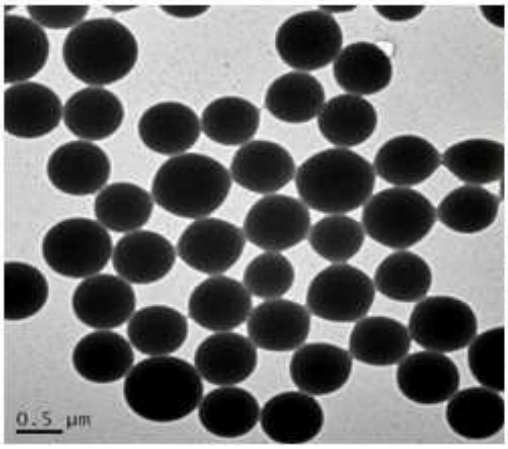


Fig.1 TEM image of PBMA microspheres

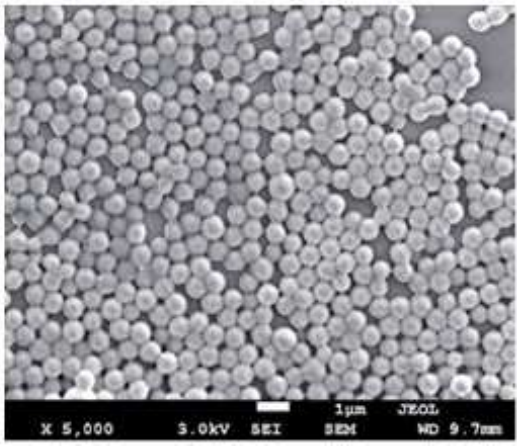


Fig.2 FESEM image of PBMA colloidal crystal template

3.3 Preparation of PBMA colloidal crystal template

Evaporation-induced self-assembly is often used to prepare the macroporous metal oxide thin films. Briefly, from a dilute nonaqueous reactant solution, the PBMA microspheres slowly deposite on substrate induced by gravity and surface tension upon solvent evaporation and exposure to air. Thus, the ordered microspheres colloidal template can be subsequently obtained. Figure 2 shows the FESEM image of the PBMA colloidal crystal template assembled on substrate by dip-drawing, indicating that the ordered array of PBMA microspheres can be formed in the large area of substrate, and there are also a small number of spaces coexisting in the template.

3.4 The thermal-decomposition behavior of template filled with $TiO_2$ precursor

It has been reported that the temperature-rise programming plays an important role on the preparation of ordered macroporous materials. During calcination in this work, the template prepared by the recipe of section "2.2.4" undergoes the processes of glass state, decomposition and oxidation, respectively. Simultaneously, anatase $TiO_2$ showing intriguing photocatalytic properties[14] is transformed by $TiO_2$ precursor. From Figure 3 it is can be seen that the first exothermal peak appears at 200℃, corresponding to the thermal decomposition of TBOT and a larger and sharper exothermal peak appears at 400℃，corresponding to the thermal decomposition of PBMA. TG curve in Figure 3 could be divided into four stages. The first stage is from room temperature to 150℃, which could be attributed to the evaporation of the physically adsorbed water and EtOH. A loss of about 10% is in the second stage from 150℃ to 270℃, which means a result of chemically transformed from $TiO_2$ precursor to $TiO_2$. The largest weight loss (about 70%) is in the temperature range from 270℃ to 430℃, indicating the process of decomposition of PBMA. There nearly did not have loss in the last stage from 430℃ to 700℃. However, Anatase $TiO_2$ is obtained at 550℃in this stage[15].

Figure 4 shows the X-ray diffraction spectrum of $TiO_2$ obtained at 550℃ by the temperature-rise programming mentioned in "2.2.4". By comparing the previous reports with respect to rutile (110) (2θ of 27.45°) and anatase (101) (2θ of 25.24°)[16], it can be concluded that the $TiO_2$ obtained in this case is mainly composed of anatase.

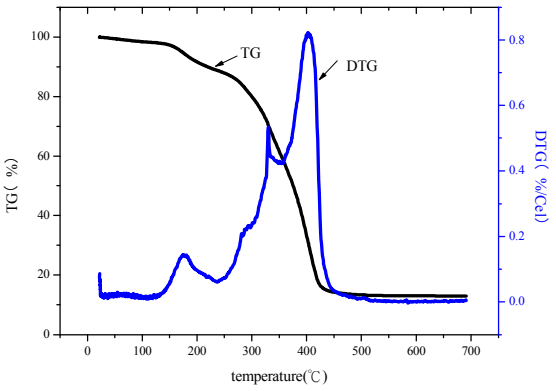


Fig.3 DTA/TG curves of template filled with $TiO_2$ precursor

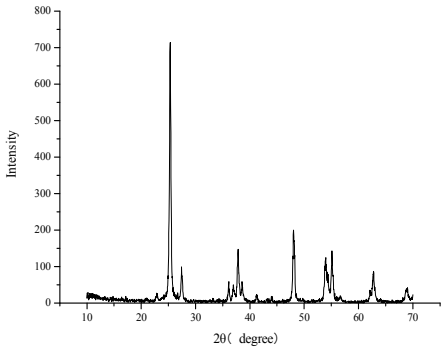


Fig.4 XRD spectrum of $TiO_2$ prepared at 550℃

3.5 Morphology of $TiO_2$ macroporous membrane

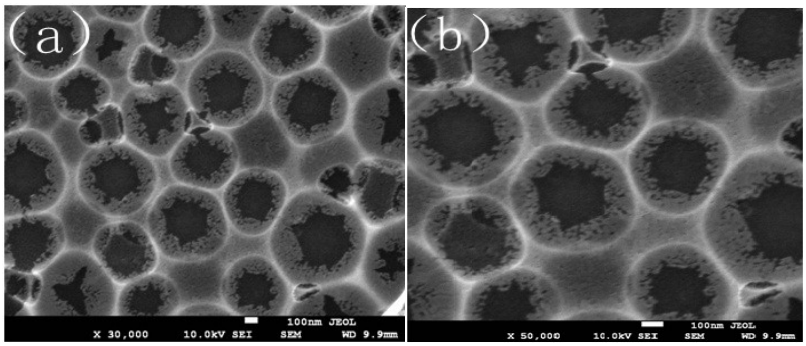


Fig.5 FESEM images of $TiO_2$ macroporous membrane (a) low-magnification (b) high- magnification

From Figure 5 it can be seen that the morphology of $TiO_2$ membrane prerared is porous structure showing a mesoscale open framework composed of $TiO_2$ wall and many holes formed by the inner PBMA cores which are burned away after calcination. Figure 5(b) also shows a few parts of the membrane are not porous structure but $TiO_2$ nanoparticles, because a small number of smaller microspheres could not be spread on the substrate. Therefore, the space held by the smaller microspheres is completely filled with $TiO_2$ sol. Furthermore, the pore size showed in Figure 5 is smaller than the microspheres showed in Figure 1, indicating the bulk shrinkage of PBMA during the processes of volatilization, decompose and calcination, respectively. On the other hand, the solidification of $TiO_2$ gel could be enlarging the pore size by annealing. Therefore the pore size could be determined by both effects of shrinkage of PBMA microspheres and $TiO_2$ solidification.

## Conclusion

In summary, a new method with Fenton reagent as a new initiator is proposed to synthesize PBMA microspheres (~500nm). The PBMA colloidal crystal templates are assembled orderly on the clean substrates of monocrystalline silicon by dip-drawing technique and $TiO_2$ macroporous membranes are prepared by using sol-dipping template method to fill the interstices among the PBMA templates, followed by calcination to remove the templates. The results show that the new method of polymerization overcomes many problems associated with the conventional emulsion

polymerization techniques such as long reaction time, necessary deoxygenation, and complicated operation. The polymerization mechanism is discussed, and the removal process of the PBMA templates and the formation of $TiO_2$ pore size are also investigated, respectively.

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