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# Templated Titania Films with Meso- and Macro- porosities **

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## Abstract

Porous $TiO_2$ films with both mesoporosity and macroporosity were fabricated by a templated sol-gel method. With incorporation of differently sized pores, the resulted structure is featured of high surface area and an aligned pore network, which are believed to be beneficial for fast charge transportation in electrolytes. The measured specific surface area and porosity of synthesized films were in range of 33-137$m^2$/g and 61-80%, respectively, depending on the size of selected template. Compared to the nanocrystalline films widely applied in current dye-sensitized solar cells (DSC), the reported structure has additional feature facilitating electrolyte diffusion and provides possible approaches towards efficient all-solid-state or quasi-solid-state junctions.

Dye-sensitized solar cells (DSC) that adopt porous $TiO_2$ film as the photoelectrode demonstrate high solar conversion efficiencies (over 10%) at competitively low costs.[1-4] Under illumination, the photon excited electron-hole pairs disassociate at the interface between $TiO_2$ and adsorbed sensitizers (dye). Free electrons are injected from sensitizers into the conduction band of $TiO_2$; while the holes are conveyed away to the counter electrode by electron transfer from electrolyte to the oxidized senstizers and subsequently electrolyte diffusion.[2] Decided by this operation mechanism, an ideal $TiO_2$ electrode is believed to possess a large surface area accessible to both dye molecules and redox species in the electrolyte. By interpenetrating a pore

network into a $TiO_2$ network, it provides pathways for both charges towards opposite electrodes after their separation. Optimal efficiency is due to balanced charge transportation ability in both ways.

Currently, doctor-blade method[1,5] and screen printing[6] are the most frequently used techniques to prepare nanocrystalline $TiO_2$ films for DSC, a process similar to the prototype DSC developed in 1991.[1] After depositing a layer of 5-50nm nanoparticles and a brief sintering at 400-500°C, porous nanocrystalline films result due to random packing of particles. The average pore size usually falls in the same range of the particle size. Though this mesoporosity (usually 50-60%) may offer a strikingly high internal surface area (e.g. a roughness factor of 460/μm),[7] the influence of the randomly tortuous and narrowed pore channels on the diffusion rate of electrolyte is believed to be negative. As pointed out by Grätzel,[6,7] a desired $TiO_2$ structure should possess a high degree of order with mesoporous channels aligned in parallel to each other and perpendicular to the electrode substrate.

Templated growth combined with sol-gel coating technique provides approaches to fabricate fine nanostructure of desired features.[8,9,15-22] Jiu and Adachi[9] reported templated growth of porous $TiO_2$ films with mixed templates of Pluronic F-127 and cetyltrimethylammonium bromide. Zukalová[8] reported a similar structure with Pluronic P-123. Both works achieved very high surface areas but with quite small pore diameters, 4-7nm[9] and 6-8nm,[8] respectively. For the concerns of mass transportation in $TiO_2$[10] and embodiment of all-solid-state or quasi-solid-state DSC, decreased pore size may present difficulties for complete coating of sensitizers (due to the relatively large molecule size of the Ruthenium based sensitizers[11]), the diffusion of redox species, and infiltration of organic hole conductor.[12] Somani[13] and Huisman[14] reported an inverse opal (IO) $TiO_2$

structure for DSC, which were composed of macropores prepared by an assemble-infiltration process. Somani[13] reported a superior performance of this IO $TiO_2$ structure in a solid-state DSC than the traditional nanocrystalline.

Inverse opal of $TiO_2$ or other materials have been reported previously[15-22] by a template-infiltration two-step process. The template particles were assembled first; then a metal organic precursor solution was infiltrated by the capillary effect. Because organic metal compounds suffer large volume shrinkage during decomposing to oxides, cracking is inevitable and a complete filling of the template by single infiltration is difficult. Repeated infiltration is necessary, which alone may take days[20] or even weeks.[17]

In this communication, we report a simply mixing-casting method for templated $TiO_2$ structures with improved film uniformity, less cracking and easier process from

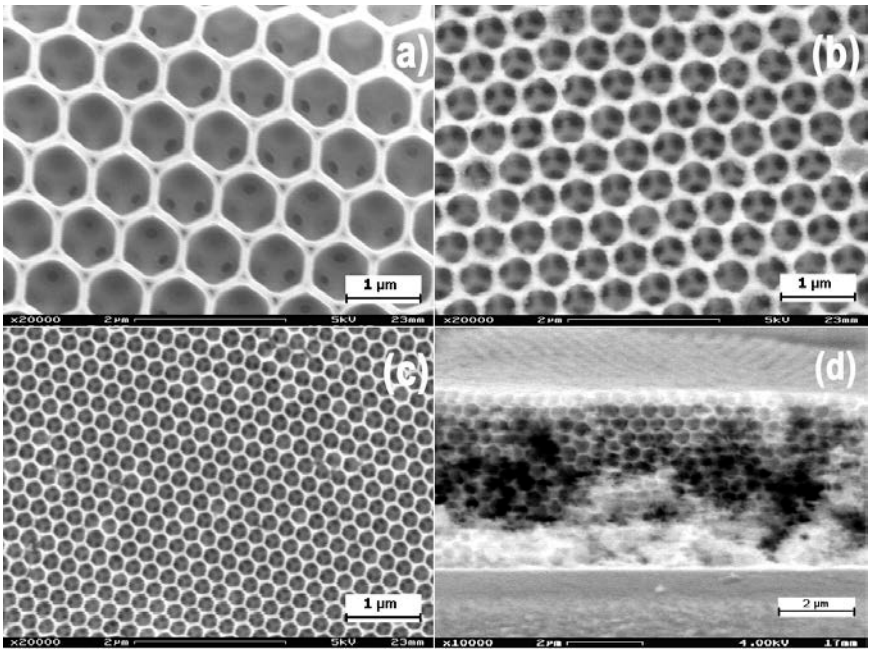


**Figure 1.** SEM micrographs of $TiO_2$ films derived from sol-gel precursor with differently sized templates. (a) 1µm; (b) 600nm; (c) 300nm; (d) Cross view of the 600nm. The coating method was cast-coating after mixing the precursor solution and PS template solution by ultrasonication for 2 minutes.

previously reported IO structures.[13,14] The preparation is also based on self-assembly of polystyrene (PS) spheres coupled with either $TiO_2$ sol-gel precursor or pre-synthesized $TiO_2$ nanocrystals (Degussa, P25, ~50nm). The developed structures show an aligned macropore network interpenetrating into a nanocrystalline film, which is capable to improve charge transport capability without significantly lowering the surface area.

Figure 1 shows the scanning electron microscope (SEM) micrographs of the synthesized porous $TiO_2$ from $TiO_2$ sol-gel precursor. The colorless and transparent sol-gel precursor was prepared by hydrolysis of titanium tetra-isopropoxide (Aldrich, 98%), and then redissolving in a certain amount of concentrated HCl. The chemical composition is similar to that of those prepared by reacting $TiCl_4$ with ice.[23] From the top views (Figure 1a-c), it can be seen that the $TiO_2$ forms a three dimensionally honeycomb-like network with an interpenetrated network of closely packed air spheres. All the pores are spatially aligned and interconnected with an average size slightly smaller than the size of PS templates. The pore size of synthesized $TiO_2$ porous films can be controlled by adopting differently sized templates with average pore size varying from 1μm to 300nm.

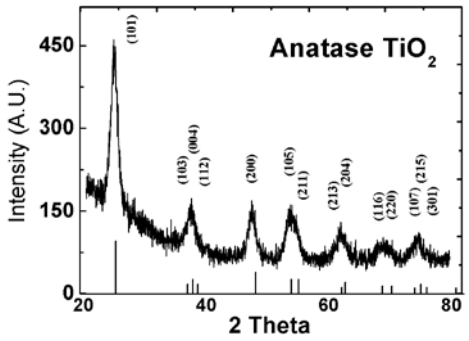


**Figure 2.** X-ray diffraction pattern of the sol-gel derived porous $TiO_2$. The lines are known anatase $TiO_2$ (JCPDS# 21-1272).

The cross-section view of the $TiO_2$ film is shown in Figure 1d. It can be observed that most of the pores in the top layers are self-assembled into a face-centered-cubic structure (A-B-C-A stacking), which is consistent with the top view observation. The pore arrangement in the lower part of the layer is suspected to have lower regularity than that of the upper part, possibly due to the substrate confinement. But all the pores are closely or nearly closely packed.

The X-ray diffraction (XRD) pattern of prepared porous $TiO_2$ film is shown in Figure 2. After annealing at 400ºC for 1 hour, pure anatase phase was obtained without observation of other phases. Varying the particle size of the template changes the specific surface area (the roughness factor), pore size and porosity of the resulted films. These factors are important for applications, such as DSC, fuel cells, electrochemical batteries, sensors and catalysts. Table 1 lists the specific surface area ($S_A$) and porosity ($P_r$) data of the $TiO_2$ films with different template sizes measured by the Brunauer-Emmett-Teller (BET) method. The samples were powders scratched off from their substrates. With size decreasing from 1μm to 160nm, the specific surface area increases from 33.2$m^2$/g to 137.2$m^2$/g. The roughness factor ($R_f$) is calculated by: $R_f = 4.2 \times (1 - P_r) \times S_A$, where 4.2 is the density of fully crystallized anatase with the unit of g/$cm^3$. The porosities of films with 300nm and 600nm pore size are higher than 70%.

**Table 1.** Specific surface area and porosity data of the synthesized $TiO_2$ films.

| Ave. pore size (nm) | Brunauer-Emmett-Teller (BET) | | |
|---|---|---|---|
| | Spec. surf. area ($m^2$/g) | Roughness factor ($\mu m^{-1}$) | Porosity (%) |
| 1000 | 33.2 | 53.7 | 61.5 |
| 600 | 60.1 | 69.7 | 71 |
| 300 | 119.1 | 148.1 | 70.4 |
| 160 | 137.2 | 197.1 | 65.8 |

Another advantage for the large pore size of this honeycomb $TiO_2$ is its potential to work with polymer electrolytes to form an all-solid-state junctions,[2,24] because polymer electrolytes usually have high viscosity and large molecular size, and thus, are difficult to be filled into tiny pores. We reproduced the honeycomb $TiO_2$ structure with pre-synthesized $TiO_2$ nanocrystals. Figure 3 shows SEM micrographs of porous $TiO_2$ films of P25 nanoparticles templated by 1μm PS nanospheres. With the P25 precursor, we observed very few cracking as shown in Figure 3a, which might be due to the negligible shrinkage of the P25 particles during heating. At high magnification (Figure 3b,c), individual P25 particles and the mesoporosity between them become distinguishable. The rest space inside the film forms an interpenetrating and aligned macropore network. Mercury porosimetry (Micromeritics, Autopore III) was adopted to investigate the pore size distribution, which is shown in Figure 4. Without templating, P25 formed

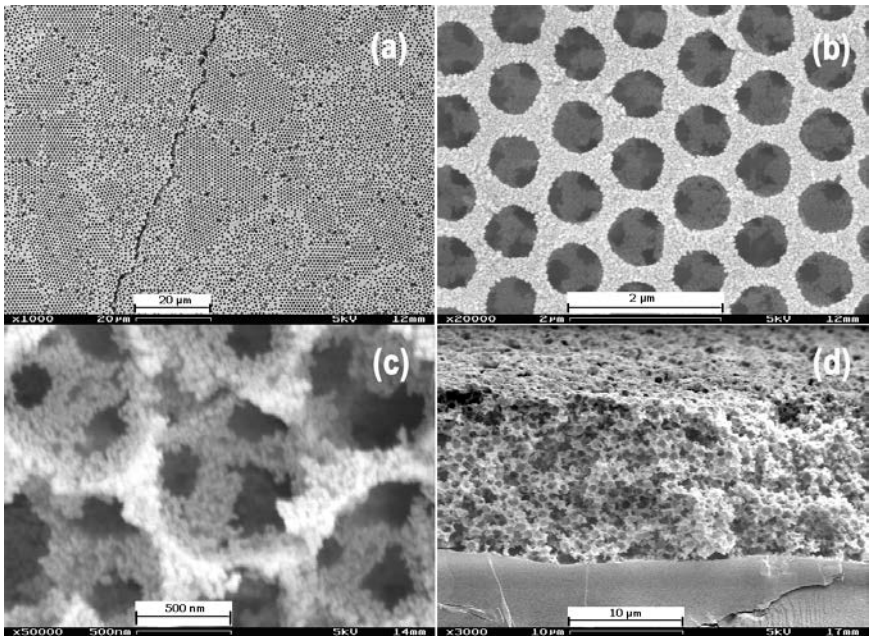


**Figure 3.** SEM micrographs of porous P25 films with both macro-and meso- porosities templated by 1μm PS at different magnifications (a) 1000×, (b) 20,000×, (c) 50,000×, (d) Cross view of a 15μm thick film.

film with an average pore size of 32nm and very narrow pore sized distribution. Templated with 1μm PS, double peaks appear in the pore volume – pore size diagram, which are centered at 35nm and 520nm, respectively. The first peak indicates preserved mesoporosity; while, the second peak proves the existence of macroporosity due to templates. The obvious size reduction of pores (530nm) from their template (1μm) is possibly due to two reasons. First, films shrink during annealing, which reduces the pore size by about 20%. Second, mercury intrusion records actually the size of pore opening, which is smaller than the pore diameter in this case.

In traditional nanocrystalline films prepared by the doctor-blade method,[1-6] the pore spaces are typically tightly constricted and some fraction of closed pore volume is inevitable, which lowers the actual surface area accessible to dyes. In the honeycomb $TiO_2$ films of this work, the large pore size and aligned pore channels make the inner surface more accessible to dyes and redox species. Considering the big size of organic

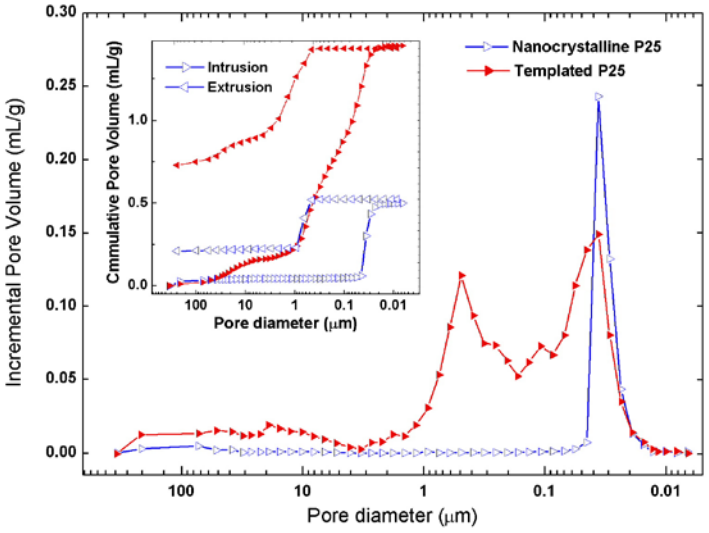


**Figure 4.** Pore size distribution of templated P25 films by mercury porosimetry. (Open triangle: non-templated P25; solid triangle: P25 templated with 1μm PS). Inset: the isotherms of both films.

hole conductors,[12] this templated P25 films show higher potential than mesoporous nanocrystalline films towards efficient all-solid-state or quasi-solid-state junctions.

We report a simple method for preparation of $TiO_2$ films with both meso- and macro-porosity. The prepared films contain aligned and closely packed pore networks. Not only high porosity, large pore size and high surface area could be achieved together, but also the flexibility to customize those parameters makes the synthesized materials promising for some applications.

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