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# Nanoporous $TiO_2$ aerogel blocking layer with enhanced efficiency for dye-sensitized solar cells

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ABSTRACT

$TiO_2$ aerogel film possessing nanoporous feature was used as the blocking layer between fluorine-doped tin oxide (FTO) substrate and mesoporous $TiO_2$ layer in dye-sensitized solar cell (DSSC). $TiO_2$ aerogel film was deposited on FTO glass via sol–gel and ambient drying processes and sintered at 500 °C, which exhibited the crystallite size of 5–25 nm, the pore size of 3–10 nm, and the thickness of ~320 nm. Brunauer–Emmett–Teller (BET) analysis confirmed its nanoporous feature and average pore size of 3.8 nm after annealing at 500 °C. In addition, $TiO_2$ aerogel film showed good interfacial adhesion with FTO and mesoporous $TiO_2$ layer, high transmittance over 70% in the visible-near infrared band, and large band gap of 3.67 eV. The DSSC device based on this aerogel blocking layer showed obviously enhanced photocurrent density ($J_{sc}$) and open-circuit voltage ($V_{oc}$) compared with the cell without blocking layer. The highest conversion efficiency of 6.0% was achieved for P25 $TiO_2$ mesoporous photoanode based on the aerogel blocking layer, improved by 36% than the control cell. The much decreased recombination frequency (aerogel cell: 11.9 Hz; control cell: 31.5 Hz) observed in Nyquist plots, together with the much prolonged electron lifetime (aerogel cell: ~1 s; control cell: 0.02–0.1 s at 0.2–0.55 V) obtained from open-circuit voltage decay curves, indicated that the increased electron life and retarded recombination at FTO/electrolyte interface were primarily responsible for the efficiency improvement in the aerogel blocking layer based DSSC.



## 1. Introduction

Dye-sensitized solar cells (DSSCs) have long been recognized as a promising alternative to conventional silicon solar cells due to their potentially high power conversion efficiency (over 10%) at a competitive cost, exceptional decoration effect, mild production process, and no use of toxic or rare metals [1–5]. Especially, the studies on DSSCs have gained a renascence in the latest years with the record efficiency reached 12.3% and 15% in succession by using novel sensitizer or electrolyte [6,7]. In a typical DSSC device, the electrons generated from photo excited dyes are injected into the conduction band of a mesoporous semiconductor photoanode (usually $TiO_2$), while the concomitant holes are transferred through the redox electrolyte to the cathode. This charge-separating process is completed by a reverse process, i.e., the recombination between photo excited electrons and the holes occurred at two interfaces, (1) the interface between $TiO_2$ nanoparticles and electrolyte in the bulk photoanode, and (2) the interface between conductive FTO and electrolyte. For the recombination occurred at $TiO_2$/electrolyte interface in the bulk photoanode, people have developed different strategies to inhibit the process, including the coating of a thin layer of $Nb_2O_5$, ZnO, $ZrO_2$, $SiO_2$, $Al_2O_3$, $In_2O_3$, MgO on $TiO_2$ nanoparticles or nanowires [8–11]. For the recombination occurred at FTO/$TiO_2$ interface, corresponding studies were much less for a long time, though it has become a routine process to deposit a thin layer of $TiO_2$ between FTO and mesoporous $TiO_2$ acting as the blocking layer [12]. Recently, people started to pay more attention on this interface. $TiO_2$ compact layer deposited by the most-used $TiCl_4$ treatment [13], sol–gel [14,15], sputtering [16], spray pyrolysis [17], and atomic layer deposition [18], and varied oxide semiconductors such as $TiO_x$ [19], Nb-doped $TiO_2$ [20], $Nb_2O_5$ [21], ZnO [22], $SnO_2$ [23], NiO [24], PbO [24], or $HfO_2$ [25] were utilized as the blocking layer. Moreover, some nanostructures or organic–inorganic hybrid structures apart from the traditional compact layer were attempted as the blocking layer, including CuO nanofibers [26], ordered mesoporous $TiO_2$ layer [27], $TiO_2$-amphiphilic diblock copolymer hybrid film [28,29], bifunctional $TiO_2$ cemented Ag grid underlayer [30] etc. In general, the blocking layer between FTO and mesoporous $TiO_2$ layer should

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be as uniform as possible to prevent the direct contact of the electrolyte with FTO, and at the same time, keep as thin as possible to reduce the interfacial series resistance. An extensive investigation of the literature showed that an average of 10–30% improvement in the power conversion efficiency could be achieved by using the blocking layer, including the notable examples of atomic-layer-deposition derived ultrathin $TiO_2$ compact layer (20% improvement) [18], Nb-doped $TiO_2$ compact layer (21.2% improvement) [20], and long-range ordered mesoporous $TiO_2$ layer (30% improvement) [27]. However, studies on the mesoporous or nanostructured blocking layers are still very rare. To our best of knowledge, there is no report on the application of nanoporous aerogel film as the blocking layer.

Aerogel is a typical nanoporous material possessing very high surface area (200–3000 $m^2/g$) [31]. After annealing at high temperature, the aerogel will lose most of the large pores (e.g. pores with the size higher than 10 nm), forming a distinguished structure with both high conductivity to electrons and high volume of disordered mesopores (less than 10 nm). In view of the success of the ordered mesoporous $TiO_2$ layer as the blocking layer of the photoanode [27], it is interesting to investigate how the aerogel layer possessing disordered mesopores influences the photoelectrochemical and recombination behavior of DSSC when used as the blocking layer of the photoanode.

In this report, we prepared $TiO_2$ aerogel film on FTO substrate via simple sol–gel and ambient-drying processes, and characterized its crystallinity, morphology, pore structures and optical properties. Then we used the $TiO_2$ aerogel film as the blocking layer of a P25 $TiO_2$ based mesoporous photoanode, and observed obviously improved power conversion efficiency (36%) compared with the control cell without the blocking layer. The underlying mechanism was probed by analyzing the microstructural and optical properties, the electrochemical impedance spectra (EIS) and open-circuit voltage decay (OCVD) curves in detail.

## 2. Experimental detail

### 2.1. Materials

Tetrabutyl titanate (TBT), acetate acid, HCl, polyethyleneglycol (PEG 400), ethanol and cyclohexane were purchased from Shanghai Chemical Reagent Corporation (China). P25 $TiO_2$ nanopowders were purchased from Degussa Co. Acetonitrile, tertbutyl alcohol, Lithium iodide (LiI, 99%), 4-tert-butylpyridine (TBP), valeronitrile, and iodine were obtained from Sigma–Aldrich Co. The ruthenium (Ru) based dye cisdi(thiocyanato)-bis(2,2-bipyridyl-4,4-dicarboxylate) ruthenium (II) (N719), 1-butyl-3-methylimidazolium iodide, guanidinium thiocyanate (GuSCN), and fluorine-doped $SnO_2$ conductive glass (FTO, sheet resistance 16 $sq^{-1}$) were purchased from Heptachroma Co. (China). All the reagents were of analytical purity and used as received.

### 2.2. Preparation of aerogel film

Acidic $TiO_2$ sol (~20 ml in volume) was prepared from TBT, ethanol and $H_2O$, with acetate acid as the chelating reagent and slight concentrated HCl as the catalyst (molar ratio of TBT: acetate acid: $H_2O$: ethanol = 1:0.62:3.91:16.90). Polyethyleneglycol (PEG 400) of 2.94 g was further added into the precursor to retard the rapid evaporation of the solvent and prevent the cracking of the film. $TiO_2$ gel film was deposited on FTO substrate via spin-coating technique, with the spinning speed of 1500 rpm and totally 3 layers of $TiO_2$ sol were applied, which produced $TiO_2$ gel film with the thickness of several micrometers. As soon as the gel film was deposited, it was transferred to the beaker containing cyclohexane for solvent exchanging at 60 °C for 1 h. And then the film was converted to aerogel film by ambient-drying for 2 h and sintering at 500 °C for 2 h. Fig. 1 illustrated the schematic preparation process of $TiO_2$ aerogel film deposited on FTO substrate. $TiO_2$ aerogel powders were prepared following the same process to determine the pore structure and the specific surface area of the corresponding aerogel film.

### 2.3. Preparation of photoanode and assembly of DSSC devices

Two photoanodes of DSSC with and without the aerogel blocking layer were prepared, denoted as $Cell_{BL}$ and $Cell_{NoBL}$. The mesoporous $TiO_2$ layer was prepared by the doctor-blade method using the slurry of commercial P25 $TiO_2$ nanoparticles ($TiO_2$ (18% by weight), ethyl cellulose (9%) and terpineol (73%). The detailed procedure was described elsewhere [12] except that the photoanode films did not treated in $TiCl_4$ solution before sensitizing. Totally one-layer of $TiO_2$ coat was applied, which generated a photoanode film with typical thickness of 7–8 μm. The photoanodes were sensitized in N719 dye solution dissolved in a mixture of acetonitrile and tertbutyl alcohol (volume ratio, 1:1) for 20–24 h at room temperature. The sensitized electrodes were sandwiched with platinized FTO electrode separated by a hot–melt spacer (40 μm in thickness, Dupont, Surlyn 1702). The internal space of the cell was filled with an electrolyte containing 0.6 mol/l 1-butyl-3-methylimidazolium iodide, 0.03 mol/l $I_2$, 0.10 M GuSCN and 0.5 mol/l 4-tertbutylpyridine in a mixture of acetonitrile and valeronitrile (volume ratio, 85:15). The active cell area was 0.239 $cm^2$.

### 2.4. Characterization

X-ray diffraction patterns were acquired from D/Max 2550 V X-ray diffractometer (Rigaku Co., Japan). Scanning electron microscope (SEM) images were recorded on a JEOL JSM-6700F scanning electron microscope operating at 10.0 kV. The $N_2$ adsorption–desorption isotherms and the pore structure were determined by a Micromeritics ASAP 2010 analyzer. Optical transmittance spectra were measured by Shimadzu UV-3101PC UV–VIS–NIR spectrophotometer, with the light beams incident from the film side, and with a bare FTO glass as the reference.

An electrochemical work station (CHI660B) and an Oriel solar simulator (91160, 300 W) were employed to characterize the photoelectrochemical performance of the cells under simulated AM 1.5 irradiation (100 mW $cm^{-2}$). *J–V* curves were measured by sweeping the bias voltage in the range of 0–0.9 V, while the electrochemical impedance spectra (EIS) were measured at $V_{oc}$ with a bias AC signal of 10 mV in the frequency range of 0.1–$10^5$ Hz. The open-circuit voltage decay (OCVD) curves were obtained by measuring the open-voltage decay with time by switching off the illumination of the solar simulator in a dark environment.

## 3. Results and discussion

$TiO_2$ aerogel film deposited on FTO substrate exhibited obscure color due to the interference of the nanoporous structure to the visible light. The film possessed good adherence to the substrate, and could not be wiped off with soft paper tissue, which was fundamentally important to act as the blocking layer of the photoanode in DSSCs. We found that the spin-coating numbers or the thickness of the wet gel film had significant effects on the quality of the aerogel film. In this study, if more than 3 layers of $TiO_2$ sol were applied, the film would crack and peel off from the substrate immediately exposed to the ambient air, which was resulted from the high internal surface tension accumulated in the film due to the rapid evaporation of cyclohexane solvent in the nanopores. Therefore, totally 3 layers of $TiO_2$ sol was spin-coated on the substrate. In addition, the PEG 400 added in the precursor played a critical role in retarding the rapid evaporation of solvent and in preventing the cracking of the aerogel film. Without PEG added, no integral aerogel film can be obtained.

We characterized the crystallinity of $TiO_2$ aerogel film using X-ray diffractometer and obtained spectrum was shown in Fig. 2a. A broad bun peak is recorded in the $2\theta$ range of 15—37°, and no diffraction peak originating from $TiO_2$ phase is detected. Because the aerogel film had been annealed at 500 °C for 2 h, which in general would form crystallized $TiO_2$ phase, we further examined the crystallinity of $TiO_2$ aerogel powders prepared following the same procedure. The pattern shown in Fig. 2b exhibits typical anatase phase of $TiO_2$ (JCPDS number: 01-0562), but the diffraction intensity is not very high. Based on these observations, we speculate that the $TiO_2$ nanoparticles in the aerogel film are also in the anatase phase, but the crystallinity is rather weak, exceeding the detecting limit of XRD analysis. Similar results were also reported in $SiO_2$–$TiO_2$ hybrid aerogel, in which selective area electron diffraction (SAED) pattern indicated nanocrystallite $TiO_2$ in anatase phase while XRD analysis showed amorphous pattern [32].

Fig. 3 illustrated SEM images of $TiO_2$ aerogel in the surface (Fig. 3a) and cross section (Fig. 3b and c). The surface of the aerogel film is fairly smooth at low resolution (not shown here), and at high resolution, typical nanoporous morphology can be observed (Fig. 3a), with the crystallite size of 5–25 nm and the pore size of