A simple template-free ‘sputtering deposition and selective etching’ process for nanoporous thin films and its application to dye-sensitized solar cells

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Abstract

A facile and straightforward method is suggested to synthesize nanoporous-TiO\textsubscript{2} thin films for dye-sensitized solar cells (DSSCs). Silver/TiO\textsubscript{2} co-sputtering led to the formation of nanocomposite films which consisted of silver nanoclusters with surrounding TiO\textsubscript{2} matrices, and metal particles were subsequently etched by just immersing in nitric acid. Nanoporous-TiO\textsubscript{2} DSSCs fabricated by this simple and effective process showed power-conversion efficiencies of up to 3.4\% at a thickness of only 1.8 \(\mu\)m, which is much superior to that of conventional nanoparticulate-TiO\textsubscript{2} DSSCs with similar thickness.

Online supplementary data available from stacks.iop.org/Nano/24/365604/mmedia

(Some figures may appear in colour only in the online journal)

1. Introduction

Nanostructured electrodes have been applied to various devices such as solar cells [1–5], lithium-ion batteries [6, 7], polymer-electrolyte-membrane fuel cells [8, 9]. In particular, the introduction of nanostructured photoelectrodes dramatically enhanced the performance of dye-sensitized solar cells (DSSCs). The amount of dye adsorbed on the device increased due to the large surface area of the nanoparticulate-TiO\textsubscript{2} photoelectrodes and, accordingly, both the photocurrent and power-conversion efficiency of the DSSC were notably enhanced [10]. Recently reported high-performance DSSCs, showing power-conversion efficiencies over 12\%, have also used this nanoparticulate-TiO\textsubscript{2} film as the photoelectrode [11].

Hydrothermally synthesized TiO\textsubscript{2} nanoparticles are conventionally used as photoelectrode materials in DSSCs. The synthesized colloidal nanoparticles are converted to viscous paste, which is then deposited on a substrate either by screen printing [12] or the doctor-blade method [13]. This conventional process guarantees high efficiencies of devices, but the process itself is time-consuming and repetitive. Other approaches to synthesize nanostructured-TiO\textsubscript{2} photoelectrodes have been suggested, such as the growth of nanorods or nanotubes [14–16], template-assisted methods [17–19], and the anodization of Ti foil [20], but they have common problems of complex and difficult experimental procedures and poor reproducibility.

Another candidate for the deposition of TiO\textsubscript{2}-photoelectrodes is by sputtering. With the merits of large-area deposition, high uniformity, and good reproducibility,
sputtering deposition has been widely utilized in the industrial field to obtain various coating layers and high-quality functional films [21]. However, TiO\(_2\) films grown by sputtering have compact structures with low surface areas, thus showing inferior properties as DSSC-photocathodes compared to the nanoparticulate-TiO\(_2\) films [22, 23]. To overcome this problem, selective etching can be directly applied. In alloy systems, electrochemically more active species are selectively etched by chemical reaction or an applied voltage, and consequently nanoporous structures composed of novel metals are synthesized [24, 25].

In this research, we introduce a facile and effective method to fabricate nanoporous-TiO\(_2\) thin films, with sputtering and subsequent selective etching. First, silver/TiO\(_2\) nanocomposite thin films were deposited by co-sputtering (left scheme in figure 1). Since the surface tension of metal is higher than that of metal-oxide [26–28], silver atoms agglomerate and form nanoclusters in the film. Then, silver nanoclusters in the nanocomposite were selectively etched in nitric acid by [24, 29]:

\[
\text{Ag} + 2\text{HNO}_3 \rightarrow \text{Ag}^+ + \text{NO}_3^- + \text{H}_2\text{O} + \text{NO}_2.
\]

The remaining TiO\(_2\) thin film with a nanoporous structure is described in the right scheme of figure 1.

2. Experimental details

Ag/TiO\(_2\) thin films were deposited on FTO glass (for DSSC fabrication) or Si(100) wafer (for x-ray analysis) by rf magnetron sputtering using Ag and TiO\(_2\) targets of 2 in diameter. Sputtering was performed in an Ar atmosphere with a working pressure of 5 mTorr at room temperature. To find the optimum conditions, the sputtering power of Ag was varied while that of TiO\(_2\) was fixed at 100 W (see supplementary data available at stacks.iop.org/Nano/24/365604/mmedia). For the comparison, bare-TiO\(_2\) thin films were also prepared with a TiO\(_2\) sputtering power of 100 W, without Ag co-sputtering.

To selectively etch Ag from Ag/TiO\(_2\) films, as-deposited Ag/TiO\(_2\) thin films were immersed in diluted nitric acid (70 wt% HNO\(_3\)/deionized H\(_2\)O, with a volume ratio of 1:2) for 1 min. The concentration of HNO\(_3\) solution (volume ratio of HNO\(_3\)/H\(_2\)O from 1:1 to 1:3) and etching time (from 1 to 10 min) did not critically influence the results in this research. HNO\(_3\)-treated films were washed in deionized H\(_2\)O and ethanol, and annealed in a box furnace at 500°C for 2 h to crystallize the remaining TiO\(_2\). The annealed films were additionally treated with an aqueous solution of titanium tetrachloride (TiCl\(_4\); Aldrich, St. Louis, USA) to improve the solar-cell performance. The experimental details for the TiCl\(_4\) treatment follow the previous research, and the dipping time is optimized in terms of the power-conversion efficiency of the DSSC [12]. Pure TiCl\(_4\) was added to pre-cooled (∼0°C) deionized H\(_2\)O to make a 40 mM TiCl\(_4\) aqueous solution, and annealed films were dipped in this solution for 1 h at 70°C. Then, TiCl\(_4\)-treated films were annealed once again at 500°C for 2 h.

To fabricate DSSCs, annealed films were immersed in 0.3 mM anhydrous ethanol solution of N719 dye (RuL\(_2\)(NCS)_2:2TBA, L = 2,2’-bipyridyl-4,4’-dicarboxylic acid, TBA = tetrabutylammonium: Solaronix) for 12 h at room temperature. The dye-adsorbed electrode and Pt thin film for the counter electrode were sealed with thermoplastic foil (Dupont), and an iodide-based redox electrolyte (AN-50: Solaronix) was injected into the gap between the two electrodes. The active area of the DSSCs was fixed at 0.36 cm\(^2\) by masking the FTO surface during the sputtering deposition.

The phase of the thin films was analyzed by x-ray diffraction (XRD, M18XHF-SRA: Mac Science, Japan). The density of the thin films was examined by x-ray reflectivity (XRR, X’pert Pro: PANalytical, Netherlands) and a simulation program (X’pert Reflectivity: PANalytical, Netherlands). XRR spectra can be simulated with the information of density, thickness, and surface roughness of the thin film, and these parameters can be obtained inversely by fitting the measured XRR spectra [30]. Field-emission scanning electron microscopy (FE-SEM, SU70: Hitachi, Japan) was used to investigate the nanostructure of thin films. In order to measure the amount of adsorbed dye on the TiO\(_2\) film, dyes were desorbed in a mixture of 0.1 M NaOH aqueous solution/ethanol with a volume ratio of 1:1, and absorption spectra of the resultant dye solutions were measured using a UV–visible spectrophotometer (Lambda 35: Perkin-Elmer, MA, USA). Photocurrent–voltage curves, electrochemical impedance spectra, and the open-circuit voltage decay of DSSCs were obtained using a solar simulator (K3000: McScience, Korea) and a potentiostat (CHI 608C: CH Instruments, TX, USA) under simulated solar illumination (AM 1.5 at 100 mW cm\(^{-2}\)). The electrochemical impedance spectra were recorded over a frequency range of 0.1–10\(^8\) Hz, where the applied bias voltage and AC amplitude were open-circuit voltage (V\(_{oc}\)) of the DSSC and 10 mV, respectively. Incident photon-to-current conversion efficiency (IPCE) spectra were obtained by using an IPCE measurement system (K3100: McScience, Korea) at a chopping speed of 5 Hz.

3. Results and discussion

3.1. Nanostructures of the thin films

X-ray diffraction (XRD) of the as-deposited Ag/TiO\(_2\) nanocomposite thin film indicates peaks from the crystalline
Figure 2. (a) X-ray diffraction (XRD) pattern of the as-deposited Ag/TiO suboxide film. Measured (black) and fitted (red) curves are superimposed. (b) XRD pattern of the nanoporous-TiO suboxide film (red) prepared by dissolution of Ag from the Ag/TiO suboxide film and subsequent annealing. For comparison, the diffraction pattern of a bare-TiO suboxide film (black) is also shown.

Ag (figure 2(a)). The grain size of Ag in the Ag/TiO suboxide nanocomposite film is calculated as ~4 nm by the Scherrer equation [30, 31], and this value is roughly verified by the transmission electron microscope (TEM) image (figure S1 at stacks.iop.org/Nano/24/365604/mmedia). Several nanocomposites with different Ag-sputtering power were also analyzed, and the grain size of Ag gets bigger as the Ag-sputtering power is increased (figure S2(a) at stacks.iop.org/Nano/24/365604/mmedia). The absence of TiO suboxide peaks in figure 2(a) and figure S2(a) (available at stacks.iop.org/Nano/24/365604/mmedia) is due to the amorphous nature in the as-deposited film. The Ag/TiO suboxide thin-film nanocomposite (figure 2(a)) was immersed in HNO3 to selectively etch Ag, and subsequent annealing at 500°C crystallized the remaining TiO suboxide (figure 2(b)). The transparency of the post-etched film in the visible range, confirmed by UV–visible spectroscopy, also demonstrates the complete removal of Ag from the Ag/TiO suboxide nanocomposite film (data not shown).

Both the electron microscope images and x-ray reflectivity (XRR) spectra confirm the formation of a nanoporous-TiO suboxide film. Figure 3(a) clearly shows the rough surface and porous morphology compared to figure 3(b), which exhibits a planar surface and compact structure of the bare-TiO suboxide film. With the same deposition time, the nanoporous-TiO suboxide film is about twice thicker than the bare-TiO suboxide film (figures 3(a) and (b)), and the selective etching of Ag did not change the thickness of the film. Furthermore, XRR simulation reveals that density of the nanoporous-TiO suboxide film is about 1.43 g cm⁻³ (figure 3(c)). This value corresponds to a film porosity of ~63%, with the assumption that the nanoporous film consists of the pure TiO anatase phase (ρanatase = 3.89 g cm⁻³). For the best performance of DSSCs, photoelectrodes should have the appropriate porosity to support sufficient space for dye adsorption on the TiO suboxide surface and provide pathways for iodide/triiodide ions in the electrolyte. The porosity of the conventional nanoparticulate-TiO suboxide electrode with the power-conversion efficiency of ~10% is approximately 65% [32], which is comparable to our nanoporous-TiO suboxide thin film.

Due to the nanoporous structure and concomitant large surface area, the nanoporous-TiO suboxide film adsorbs much more dye than the bare-TiO suboxide film, as shown in figure 4. The amount of dye adsorbed on the nanoporous-TiO suboxide film (0.7 µm thick, figure 3(a)), calculated from UV–visible absorption spectra in figure 4, is 2.26 × 10⁻⁸ mol cm⁻², and the corresponding surface area of the nanoporous film is 231.4 m² g⁻¹ (table 1), assuming that a single dye molecule adsorbs on TiO suboxide within 1.7 nm³ [1]. Since the conventional nanoparticulate-TiO suboxide photoelectrode has a surface area of ~80 m² g⁻¹ [32], the nanoporous-TiO suboxide film is expected to contain much more dye and thereby exhibits improved solar-cell properties. In addition, the average pore size in the nanoporous-TiO suboxide film is estimated to be 7.7 nm (table 1), with the cylindrical pore-shape assumption [33] which is generally used to determine the nanoporosity in DSSCs. Although the calculated pore size is smaller than that of the typical nanoparticulate-TiO suboxide film, it is supposed that this value is sufficient for iodide/triiodide ions in the electrolyte to operate DSSC normally [34].

3.2. NaNanoporous-TiO suboxide thin films as photoelectrodes of DSSC

The nanoporous-TiO suboxide thin-film DSSC exhibits much enhanced solar-cell properties to those of the bare-TiO suboxide thin-film DSSC (dashed lines in figure 5 and table 2). The higher power-conversion efficiency (η) of nanoporous-TiO suboxide DSSCs is mainly attributed to the increased current density, and this is consistent with the dye-loading data (figure 4). There are no noticeable differences in solar-cell properties among the DSSCs with different Ag-sputtering power (figure S2(b) at stacks.iop.org/Nano/24/365604/mmedia), and nanoporous-TiO suboxide films for thicker DSSC were prepared with a Ag-sputtering power of 15 W. However, the DSSC with thicker nanoporous-TiO suboxide film (1.8 µm) does not reach the expected current density and η (red solid line in figure 5), in spite of the increased dye loading proportional to the TiO suboxide thickness (data not shown).

The electron diffusion length (Dₑτ)¹/² in DSSCs influences the collection of photoelectrons. The electron diffusivity (Dₑ) of 1.8-µm-thick nanoporous-TiO suboxide DSSC,
Figure 3. Cross-sectional FE-SEM images of (a) the nanoporous-TiO$_2$ film and (b) the bare-TiO$_2$ film. X-ray reflection spectra of (c) the nanoporous-TiO$_2$ film and (d) the bare-TiO$_2$ film. Simulated spectra (red) are shown with the measured spectra (blue) in both (c) and (d). For both analyses, films were deposited on Si(100) wafers. The deposition time was the same for the nanoporous- and bare-TiO$_2$ film.

Table 1. Porosity, surface area, and average pore size of the nanoporous-TiO$_2$ film. The values of the conventional nanoparticulate-TiO$_2$ film are also listed for comparison.

<table>
<thead>
<tr>
<th></th>
<th>Porosity (%)</th>
<th>Surface area (m$^2$ g$^{-1}$)</th>
<th>Average pore size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nanoporous TiO$_2$</td>
<td>63.2$^a$</td>
<td>231.4$^b$</td>
<td>7.7$^c$</td>
</tr>
<tr>
<td>Conventional nanoparticle TiO$_2$</td>
<td>65.3$^d$</td>
<td>86.0</td>
<td>20.2</td>
</tr>
</tbody>
</table>

$^a$ Calculated, with the assumption that the film consists of pure anatase phase ($\rho_{\text{anatase}} = 3.89$ g cm$^{-3}$).

$^b$ Calculated, with the assumption that a single dye molecule adsorbs on the TiO$_2$ surface with an area of 1.7 nm$^2$.

$^c$ Calculated, with the cylindrical pore-shape assumption [33].

$^d$ Values are referred from [32].

Table 2. Short-circuit current ($J_{sc}$), open-circuit voltage ($V_{oc}$), fill factor, and power-conversion efficiency ($\eta$) values of various thin-film TiO$_2$ DSSCs.

<table>
<thead>
<tr>
<th></th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>$V_{oc}$ (V)</th>
<th>Fill factor (%)</th>
<th>$\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bare TiO$_2$ (0.35 µm thick)</td>
<td>0.77</td>
<td>0.750</td>
<td>55.2</td>
<td>0.32</td>
</tr>
<tr>
<td>Nanoporous TiO$_2$ (0.7 µm thick)</td>
<td>2.58</td>
<td>0.793</td>
<td>66.2</td>
<td>1.35</td>
</tr>
<tr>
<td>Nanoporous TiO$_2$ (1.8 µm thick)</td>
<td>4.23</td>
<td>0.781</td>
<td>66.2</td>
<td>2.19</td>
</tr>
<tr>
<td>TiCl$_4$-treated nanoporous TiO$_2$ (1.8 µm thick)</td>
<td>7.29</td>
<td>0.750</td>
<td>62.7</td>
<td>3.43</td>
</tr>
</tbody>
</table>

Obtained from the Nyquist plot at $V_{oc}$ (figure 6(a)) [35], it is two orders of magnitude smaller than that of the conventional nanoparticulate-TiO$_2$ DSSC ($\sim 3 \times 10^{-5}$ cm$^2$ s$^{-1}$) [35, 36], and the corresponding ($D_e \tau$)$^{1/2}$ is 1.24 µm (τ $\equiv 35$ ms from $\tau = (2\pi f)^{-1}$, where $f$ stands for the frequency at the arc peak in the Nyquist plot [37]). This calculation indicates that the 1.8-µm-thick nanoporous-TiO$_2$ DSSC has a problem with charge collection since the photoelectrode is thicker than its ($D_e \tau$)$^{1/2}$. The charge-collection efficiency ($\eta_{cc}$) in DSSCs can be calculated by:

$$\eta_{cc} = (1 + \tau_{tr}/\tau)^{-1},$$

where $\tau_{tr}$ is the electron-transport time in the photoelectrode ($\tau_{tr} = d^2/2.5D_e$ with $d$ for the photoelectrode thickness) [1, 38]. The value of $\eta_{cc}$ in the 1.8-µm-thick nanoporous-TiO$_2$ DSSC is 54%, considering that half of the photogenerated electrons recombine before reaching the FTO electrode.

Since ($D_e \tau$)$^{1/2}$ in DSSCs is directly proportional to ($R_{rec}/R_{tr}$)$^{1/2}$ (where $R_{rec}$ and $R_{tr}$ represent the electron-recombination and electron-transport resistance at the photoelectrode, respectively) [39, 40], it is suggested that loss of photoelectrons via recombination reactions and slow photoelectron transport would be more dominant in the
Figure 4. Absorption spectra of desorbed dye solutions from the nanoporous-TiO$_2$ film (red) and the bare-TiO$_2$ film (black). Photo of dye-adsorbed TiO$_2$ films is shown in the inset.

Figure 5. Photocurrent–voltage ($J$–$V$) characteristics of DSSCs.

nanoporous-TiO$_2$ DSSC ($(D_e \tau)^{1/2} = 1.24 \mu$m), compared with the typical nanoparticulate-TiO$_2$ films ($(D_e \tau)^{1/2} \approx$ several $\mu$m [35, 41]). The shorter $(D_e \tau)^{1/2}$, and therefore defectiveness, are attributed to the smaller pore size (table 1) and more grain boundaries. Furthermore, oxygen vacancies, hydroxyl groups, and coordinated Ti atoms are known to act as recombination centers at the surface of TiO$_2$ [42, 43], so passivation of these defects can increase $R_{\text{rec}}$ and decrease $R_{\text{tr}}$ at the same time.

The formation of an additional sub-nm-thick TiO$_2$ layer by TiCl$_4$ treatment, which is widely used in the DSSC-field to increase $\eta$ [32, 44], is expected to alleviate various surface defects of our nanoporous-TiO$_2$ film [45]. O’Regan’s group systematically studied the effects of TiCl$_4$ treatment on the photoelectrode of DSSC and observed a reduction of recombination rate, which is equivalent to an increase of $R_{\text{rec}}$ [41, 46]. In addition, the growth of TiO$_2$ nanocrystallites by the TiCl$_4$ treatment also improves the $R_{\text{rec}}/R_{\text{tr}}$ ratio. Indeed, $D_e$ of the nanoporous-TiO$_2$ film is enhanced by more than one order of magnitude through the TiCl$_4$ treatment (figure 6(a)), and the corresponding $(D_e \tau)^{1/2}$ is improved to 3.21 $\mu$m. As a result, $\eta_{\text{cc}}$ increases to 88% (from 54% before the TiCl$_4$ treatment), which means that the photoelectron collection of nanoporous-TiO$_2$ DSSC is significantly improved by the TiCl$_4$ treatment. Electron lifetimes ($\tau$) deduced from open-circuit voltage ($V_{\text{oc}}$) decays [47] also show the effects of TiCl$_4$ treatment on the photoelectron-transport properties (figure 6(b)).

With the TiCl$_4$ treatment, the short-circuit current ($J_{sc}$) and $\eta$ of the 1.8-$\mu$m-thick nanoporous-TiO$_2$ DSSC increased by 72% and 57%, respectively (figures 5, 7(a), and table 2), despite the reduced dye loading (figure 7(b)). In the conventional nanoparticulate-TiO$_2$ DSSCs, the increase of dye loading induced by an enlarged actual surface area has been suggested as one of the enhancement mechanisms resulting from the TiCl$_4$ treatment [32, 44]. In contrast, the TiCl$_4$ treatment shrinks the pores in the nanoporous-TiO$_2$ photoelectrode, and therefore both the surface area and the amount of adsorbed dye decrease (figure 7(b)). The IPCE at
Figure 7. Effects of TiCl$_4$ treatment on the 1.8-μm-thick nanoporous-TiO$_2$ electrode. (a) Incident photon-to-current conversion efficiency (IPCE) spectra of nanoporous-TiO$_2$ DSSCs. (b) Absorption spectra of desorbed dye solutions from TiCl$_4$-treated nanoporous-TiO$_2$ film (blue) and non-treated nanoporous-TiO$_2$ film (red).

an arbitrary wavelength $\lambda$ can be expressed as [48]:

$$\text{IPCE}(\lambda) = \text{LHE}(\lambda)\varphi_{\text{inj}}\eta_{\text{cc}},$$

where LHE(\lambda) is the light-harvesting efficiency and $\varphi_{\text{inj}}$ is the quantum yield for electron injection from dye to photoelectrode. The TiCl$_4$ treatment led to the enhancement of IPCE over the whole wavelength range (figure 7(a)) in spite of the decreased dye loading and thus lower LHE (figure 7(b)), and these results qualitatively indicate that the increased photocurrent following the TiCl$_4$ treatment comes from the enhancement of $\eta_{\text{cc}}$ ($\varphi_{\text{inj}} \cong 1$ for N719 dye-TiO$_2$ system [48]). Finally, a power-conversion efficiency of 3.43% is attained with the 1.8-μm-thick nanoporous TiO$_2$ thin film—a value much superior to that of DSSCs fabricated by the conventional TiO$_2$-nanoparticle method with similar thickness. (The average $\eta = 2.25\%$ at 1.5 μm [49] and $\eta = 1.08\%$ at 1.1 μm [50], without the TiCl$_4$ treatment. We consider that enhancement due to the TiCl$_4$ treatment in the nanoparticulate-TiO$_2$ DSSCs is generally 10–20$\%$ [33, 44].)

4. Conclusions

We have developed a straightforward and effective method to fabricate nanoporous-TiO$_2$ thin films using co-sputtering and selective etching. Our nanoporous-TiO$_2$ thin films were applied to the photoelectrode of DSSCs, and showed power-conversion efficiencies of up to 3.4% at a thickness of just 1.8 μm. The nanoporous-TiO$_2$ film exhibited a porosity of ~63%, a value comparable to typical nanoparticulate-TiO$_2$ films used in DSSCs. However, the surface area of our nanoporous-TiO$_2$ film was calculated as ~230 m$^2$ g$^{-1}$, which is three times greater than that of the nanoparticulate-TiO$_2$ film. The TiCl$_4$ treatment on the nanoporous-TiO$_2$ photoelectrode led to the effective collection of photoelectrons, and thereby both the photocurrent and power-conversion efficiency of the DSSC were enhanced in spite of the reduced dye loading. We expect that this technique can be utilized for large-scale deposition of photoelectrodes and mass production of sensitized solar cells. Furthermore, not limited to TiO$_2$ and sensitized solar cells, nanoporous thin films with various materials and for diverse purposes can be fabricated through this facile technique.

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References

Fig. S1. TEM image of the Ag/TiO$_2$ nanocomposite film.
Fig. S2. (a) XRD patterns of Ag/TiO$_2$ nanocomposite films and (b) photocurrent density-voltage ($J$-$V$) characteristics of DSSCs with different Ag sputtering power.