<table>
<thead>
<tr>
<th>Title</th>
<th>Development of a Novel High Efficiency Dye-sensitized Solar Cell Using ZnO Based Electrodes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Author(s)</td>
<td>HOU, Shengwen</td>
</tr>
<tr>
<td>Citation</td>
<td>高知工科大学　博士論文</td>
</tr>
<tr>
<td>Date of issue</td>
<td>2017-03</td>
</tr>
<tr>
<td>URL</td>
<td><a href="http://hdl.handle.net/10173/1511">http://hdl.handle.net/10173/1511</a></td>
</tr>
<tr>
<td>Rights</td>
<td>Text version ETD</td>
</tr>
</tbody>
</table>

Kochi, JAPAN
http://kutarr.lib.kochi-tech.ac.jp/dspace/
Dye-sensitized solar cell (DSSC) has attracted extensive attention and been considered as a promising candidate for the next generation solar cell due to its advantages such as low-cost, relatively simple fabrication process, and environmentally friendly materials. Since DSSC was invented by Prof. M. Graetzel and Dr B. O’Regan in 1991, it has gained more and more research attention all over the world in over last 25 years. Until now, the highest conversion efficiency of DSSC reported by Graetzel’s group has reached around 15% [1]. However, the development of DSSC has encountered the bottleneck in the improvement of conversion efficiency. The reason are small surface area and low transportation of TiO₂ based photoanode, low photoelectric conversion of dye, and corrosion of redox electrolyte etc.

Photoanode is one of the most important parts for DSSC. Photoanode is composed of the photoanode material and transparent conductive oxide (TCO) substrate. High transmittance and large surface area for dye absorption are the basic requirement for photoanode material. TiO₂ is the most common photoanode material used in DSSCs. Anatase TiO₂ has a better photovoltaic performance than other phases due to its larger bandgap. However, TiO₂ is difficult to obtain textured structure to absorb more dye molecules. The low electron mobility (i.e. 0.1~4 cm²/(V·s)) of TiO₂ causes low transportation during electron transportation from TiO₂ to substrate. These limitations influence the conversion efficiency of TiO₂-based DSSC. Compared with TiO₂, ZnO has similar energy bandgap (3.3 eV) with TiO₂ (3.2 eV). However, ZnO has much higher electron mobility (i.e. 200~1000 cm²/(V·s)) than TiO₂. In addition, ZnO is much easier to be fabricated into nanostructures. Therefore, ZnO is one of the most promising alternative photoanode materials for DSSC.

ITO or FTO are the most common TCO substrates. However, vertical alignment of ZnO nanorods could not be well controlled on ITO or FTO due to large lattice mismatch [2]. Therefore, suitable TCO substrates should be studied to replace ITO or FTO. Based on our previous research [2-4], fabrication of vertical aligned ZnO nanorods was still not well studied. The growth mechanism of vertical aligned ZnO nanorods should be further investigated. Furthermore, ZnO-based electrodes have high electron recombination and low stability in acidic electrolyte, which limited the improvement of ZnO based DSSC.

Therefore, in order to solve above problems, we designed a novel photo electrode structure. ZnO nanorods were fabricated on ZnO based substrates which was expected to fabricate ZnO nanorods with good crystallinity, good vertical alignment and large surface area. Additionally, anatase TiO₂ shell was coated on ZnO nanorods with the purpose to reduce recombination and stability.

In my research, there are several novel ideas to improve performance of ZnO based DSSC.
1) Aluminium or gallium doped ZnO substrates with low resistivity and high transmittance were deposited to replace ITO. The effects of metal doping on crystallinity, resistivity and transmittance was investigated.

2) Vertical alignment of ZnO nanorods was controlled on ZnO based substrates to improve optical transmittance and crystallinity. The growth mechanism of vertical aligned ZnO nanorods was investigated.

3) Anatase TiO$_2$ shell was coated on ZnO nanorods to reduce electron recombination. The mechanism of TiO$_2$ film reducing the recombination was investigated.

The main work will be discussed in terms of fabrication of transparent conductive ZnO based substrates, vertical alignment controlling on ZnO based substrates, and fabrication of ZnO-TiO$_2$ core-shell nanorods.

1. **Deposition of transparent conductive ZnO based substrates**

   Transparent conductive substrates should not only have low resistivity, high optical transmittance and high electron mobility, but also contribute to the vertical alignment of ZnO nanorods. However, common substrates such as ITO could not contribute to the vertical alignment of ZnO nanorods due to large lattice mismatch. Therefore, transparent conductive substrates with low lattice mismatch were studied.

   Transparent conductive AZO and GZO films were deposited by sputtering system with optimized deposition conditions. The aluminium and gallium dopant not only improved the crystallinity of ZnO film, but also the resistivity and electron mobility. Film thickness dependence on structural, optical and electrical properties of films was investigated. It was found that as film thickness increased from 50 to 300 nm, the crystallinity of AZO and GZO films was improved, resistivity decreased, and electron mobility increased. 300 nm-thick AZO films showed lowest resistivity of $6.23 \times 10^{-4}$ Ω·cm, highest mobility of 18.1 cm$^2$/(V·s) and high optical transmittance of 85%, which were comparable to commercial ITO substrate of Sigma-Aldrich Co. Ltd (a resistivity of $3 \times 10^{-4}$ Ω·cm, a mobility of 20 cm$^2$/(V·s) and optical transmittance of 84%). Moreover, (0001) orientation growth was controlled for AZO and GZO films.

   In summary, 300 nm-thick ZnO based substrates could replace ITO substrate to be used as transparent conductive layers for electrode of DSSC. The deposited ZnO based substrates were controlled to be (0001) orientation.

2. **Vertical alignment controlling of ZnO nanorods on ZnO based substrates during multi-annealing process**

   In order to pass more phonons through electrode to dye molecules, high transmittance was required for both substrate and ZnO nanorods. Therefore, ZnO nanorods should be fabricated in vertical alignment to reduce the light scattering and absorption. The vertical alignment of ZnO
nanorods was influenced by the substrates. Our research verified that lattice mismatch between substrate and ZnO nanorods influenced the vertical alignment. Therefore, ZnO nanorods fabricated on ZnO based substrates should be investigated.

Multi-annealing process was developed to fabricate ZnO nanorods. The influence of substrates including AZO, GZO, and ITO substrates on the growth of ZnO nanorods was investigated. It was found that ZnO nanorods fabricated on ZnO based substrates were vertical alignment while those fabricated on ITO substrate were not vertical aligned. The calculated lattice constant $c$ showed lattice mismatches between ZnO nanorods and AZO film, ZnO nanorods and GZO, ZnO nanorods and ITO substrate were 0.048%, 0.035%, and 70.35%, respectively. Low lattice mismatch contributed to the vertical alignment of ZnO nanorods. During multi-annealing process, ZnO film was reduced to zinc and ZnO nuclei formed on the surface of ZnO film. ZnO nuclei would follow the same (0001) growth direction with ZnO based substrates according to minimum energy principle. Due to (0001) orientation was the polarization direction of ZnO, ZnO nanorods would prefer to grow along this orientation. Therefore, vertical alignment of ZnO nanorods was well controlled, which had high optical transmittance.

In summary, the growth direction of ZnO nanorods followed the same vertical growth direction with underneath ZnO based substrate due to the low lattice mismatch between ZnO nanorods and substrate. Vertical alignment of ZnO nanorods improved optical transmittance.

3. **Vertical alignment controlling of ZnO nanorods on ZnO based substrates during chemical bath deposition.**

Chemical bath deposition (CBD) is a low-temperature method to fabricate ZnO nanorods. During CBD process, substrates served as the seed layer for ZnO nanorods. Vertical alignment of ZnO nanorods was largely influenced by the substrates. Therefore, vertical alignment of ZnO nanorods in CBD method should be studied.

Different substrates including AZO, GZO, ITO and glass were used as seeds layers to grow ZnO nanorods by CBD method. It was found that vertical alignment of ZnO nanorods was obtained on AZO and GZO substrates while that was not obtained on ITO and glass substrates. During CBD process, ZnO nanorods grew at AZO and GZO substrates, which served as seed layers. As well known, (0001) orientation is the polarization direction of ZnO nanorods. Because ZnO based substrates had good (0001) orientation, formed ZnO would follow the same (0001) growth direction due to homogenous growth. As growth time increased, ZnO nanorods would prefer to grow vertically on ZnO based substrates. Moreover, the effects of AZO film thickness, precursor concentration and growth time on growth of ZnO nanorods were investigated. As thickness of AZO film increased, the diameter of ZnO nanorod increased due to the increasing grain size of AZO film. As precursor molecule concentration ratio increased, the growth of ZnO nanorods was suppressed. As growth time expanded, ZnO nanorods kept the same (0001) orientation with AZO film.
In summary, ZnO nanorods followed the same (0001) growth direction with ZnO based substrates due to homogenous growth. Therefore, vertical alignment of ZnO nanorods was controlled on ZnO based substrates by CBD method.

4. **Fabrication of ZnO-TiO$_2$ core-shell structure.**

Even though our fabricated ZnO based electrodes had many advantages such as high transportation rate, high transmittance and large surface etc., The performance of ZnO based DSSC was limited by high electron recombination, low stability in acidic electrolyte solution, and formation of Zn$^{2+}$/dye complex on the surface. In order to overcome these disadvantages, ZnO nanorods should be coated with a chemically stable shell. Anatase TiO$_2$ had similar bandgap to ZnO, which meant electron could easily transport from TiO$_2$ to ZnO. Anatase TiO$_2$ was more chemically stable and had low electron-hole recombination, which would greatly improve the performance of ZnO based electrodes. Therefore, anatase TiO$_2$ was coated on ZnO nanorods.

TiO$_2$ film was synthesized on ZnO nanorods using titanium tetraisopropoxide (TTIP) as titanium source by mist-CVD method. It was found that pure anatase TiO$_2$ film with very uniform surface could be synthesized by mist-CVD method. The anatase to rutile transformation temperature of TiO$_2$ films was over 1000 °C, which meant this TiO$_2$ film had very high thermal stability. Anatase TiO$_2$ shell had a significant influence on the efficiency ZnO based DSSC. As mist-CVD reaction time increased, the anatase crystallinity of TiO$_2$ shell was increased and the optical transmittance was decreased due to the increasing thickness of TiO$_2$ shell. After coated with TiO$_2$ shell, short circuit current density ($J_{sc}$) and fill factor (FF) of ZnO based DSSC was significantly improved. The conversion efficiency of ZnO based DSSC was twice improved after coated with TiO$_2$ shell.

Anatase TiO$_2$ shell had similar bandgap with ZnO nanorods, which meant electrons could easily transmit from conductive band of TiO$_2$ to that of ZnO. For ZnO-TiO$_2$ core-shell structures, electron was ejected from the LUMO of dye molecule to the conductive band of TiO$_2$ shell and then transmitted to that of ZnO nanorods. Because of the barrier between TiO$_2$ shell and ZnO nanorods, the electron-dye and electron-I$_3^-$ recombination was greatly suppressed. Furthermore, because electron mobility in ZnO was much faster than that in TiO$_2$, the electron transportation from dye to conductive band of TiO$_2$ and then through ZnO nanorods to AZO substrate was significantly improved. Therefore, the TiO$_2$-ZnO core-shell greatly improved $J_{sc}$ and FF.

In summary, ZnO-TiO$_2$ core-shell nanorods was verified to help utilize electron mobility and diffusion rate of ZnO nanorods as well as the low recombination of TiO$_2$. Low electron recombination and fast electron mobility of ZnO nanorods improved the electron transportation for TiO$_2$-ZnO core-shell nanorods. Therefore, the efficiency of ZnO based DSSC was greatly improved after coating anatase TiO$_2$ shell.

Reference

