CHAPTER 3

Two-Step Coating-Texturing Process of ZnO Photoelectrodes

A simple technique for increasing J_{sc} is an increment of ZnO films thickness. It is well known that thick films give a high volume for dye adsorption in photoelectrodes. Thus, J_{sc} will be increased and resulting an enhancement of PCE. However, thicker films are a problem in ZnO/dye/electrolyte interfaces. It inhibits regeneration process due to a difficulty of electrolyte penetration into deeper layer which is result to a low FF. To avoid this effect, thinner films (in order of nanometer) are introduced to improve the electrolyte flexibility. But, the J_{sc} is decreased because the thin films are not supported a high dye adsorption. To solve the involving factors, the J_{sc} and FF are improved using two-step coating-texturing process. The thick films are prepared using two-step coating process to support more dye adsorption for solving the J_{sc} problem. For solving the FF problem, the films are texturing using two-step texturing process to form a porous structure. A double of sequential coating and texturing process called "two-step coating-texturing process" in this work.

3.1 Two-step coating-texturing process

A two-step coating-texturing process is illustrated in Figure 3.1. ZnO paste was coated onto FTO substrate and annealing to form ZnO films for the 1^{st}-step coating process. After cooling down, the films were texturing by immersing into a bath of acid solution for 10 s, rinsed and annealed for the 1^{st}-step texturing process. The films were repeating coating and for the 2^{nd}-step coating process. Finally, the films were texturing for the 2^{nd}-step texturing process with base solution for 1-3 min, rinsed and annealed to complete the two-step coating-texturing process. The two-step coating-texturing films are defined as ZnO(acid 10 s)/ZnO(base x min), while the x is a texturing time for base solution.

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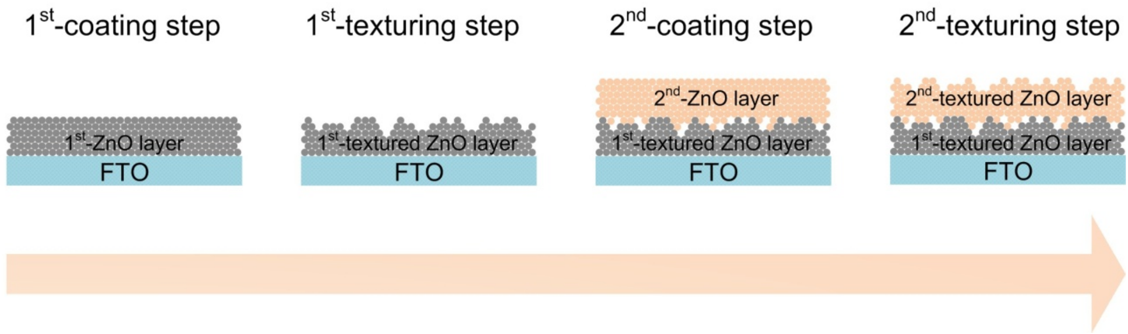

Figure 3.1 An illustration of two-step coating-texturing process of ZnO photoelectrodes. Reproduced with permission from ref [73]. Copyright (2015) Elsevier.

3.2 Morphology

Figure 3.2 show morphologies of two-step coating-texturing ZnO films using acid and base solutions for the 1st and 2nd-texturing step, respectively. Two-step coating (ZnO/ZnO) films were prepared for comparative investigation. The ZnO/ZnO films show a rough morphology as similar to the one-step texturing films (see Figure 2.1). For two-step coating-texturing films, the morphology shows small changed as seen in Figure 3.1(b)-(d). The change in surface is appeared likely to the one-step texturing (ZnO) films by base solution in each the texturing time. From the result, it can be assumed that morphology changes a relation to the 2nd-texturing step of base solution.

Additional to cross-sectional images in Figure 3.3, the ZnO/ZnO films show a significant increment in thickness of 44.04 ± 0.94 μm which is greater than ZnO films (see Figure 2.2) as an expectation. However, the films formation exhibits a non-homogenous films which can be seen a large junction between the first and the second layers.

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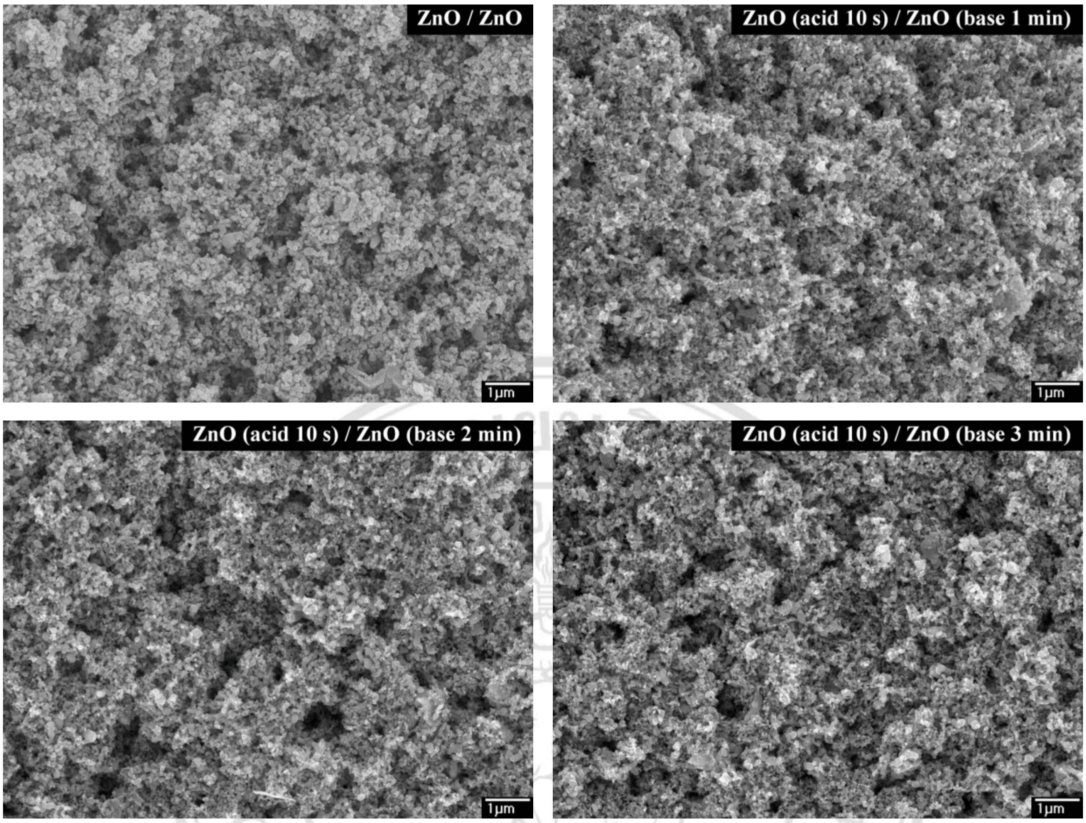

Figure 3.2 Morphology of two-step coating-texturing films.

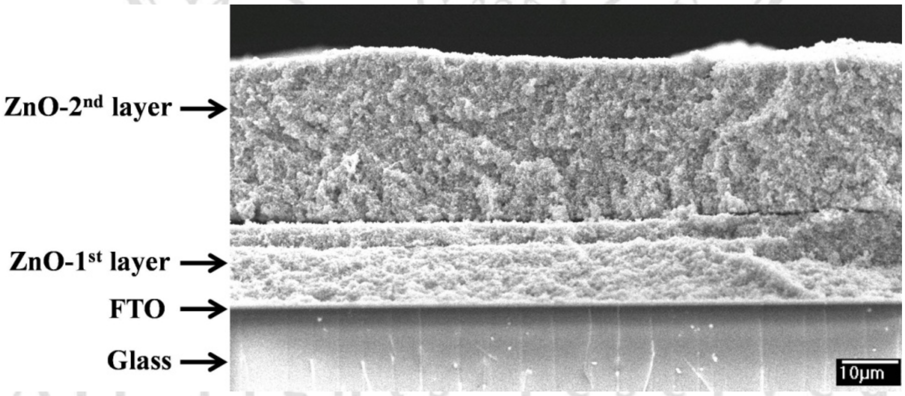

Figure 3.3 Cross-sectional FE-SEM images of the two-step coating films.

3.3 Pore analysis

To carefully observe the morphology, image processing analysis using image-J software is used for analyzing surface pore characterization. Figure 3.4 shows pore area and pore density of the films and the analyzed values are listed in Table 3.1. A minimum calculating pore area of 56.70% is observed for ZnO/ZnO films. After the modification using two-step coating-texturing process, the films show an increase in pore area directly related to the texturing time. This result might be due to aggregate particles removal during the process. The pore density displays a slightly increase for short texturing time (1-2 min) similar to the trends of pore area. However, a rapid reduction is occurred for long texturing time (3 min), which suggest that an optimization of the pore area and the pore density can be carried out by two-step coating-texturing process with a short texturing time.

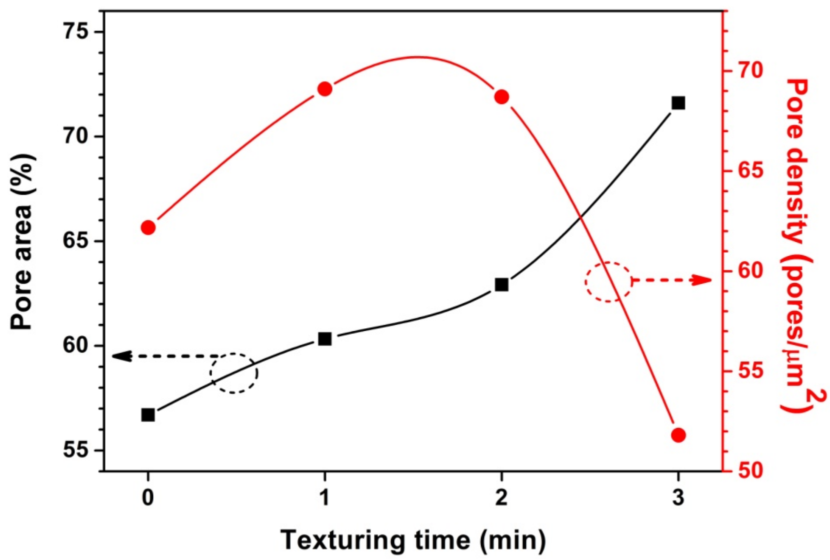

Figure 3.4 Pore area and pore density of two-step coating-texturing films with different texturing time for the second texturing step.

Table 3.1 Pore area and pore density of two-step coating-texturing films.

Films	Pore area (%)	Pore density (pores/μm^2)
ZnO/ZnO	56.70	62.18
ZnO (acid 10 s) / ZnO (base 1 min)	60.33	69.10
ZnO (acid 10 s) / ZnO (base 2 min)	62.92	68.71
ZnO (acid 10 s) / ZnO (base 3 min)	71.60	51.81

3.4 Mapping profile analysis

To investigate a relative pore deep, mapping profiles were analyzed using image-J software. The ordinary FE-SEM images were processed; convert of gray scale with 8-bits (image >> type >> 8-bit), threshold adjustment (image >> adjust >> threshold >> auto), then mapping the surface (analyze >> plot profile). The mapping profiles are shown in Figure 3.5. In the analysis, a real deep of pore is not performed in the analyzing profile. Only a relative deep is mentioned to compare texturing effects on the films for a different texturing time, and a difference between peak and trough profiles means a relative deep of the pore. From the mapping profiles, increase in relative deep is found after the texturing process in comparison to the ZnO/ZnO films. Moreover, the deep increases as increasing the 2nd-texturing time implied that the chemical corrosion removes aggregate particles from the surface.

In addition, pore histogram was analyzed to investigate a relative deep of pore formation. Fig. 3.6 shows histograms in term of gray scale level, the level ranges are in 0 – 255 where the level 0 and 255 means a relative deepest pore formation and a relative non pore (planar surface), respectively. It is found that the gray scale level at the maximum pore count frequency shifts to a lower level for two-step coating-texturing films compare to the ZnO/ZnO films. It can be assumed an increased relative pore deep

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due to a long duration for chemical reaction. The aggregate particles at the surface are firstly removed and deeper particles at deeper layer are continuous removed for the long texturing time after the first layer removal. From the result, it is believed that the deeper pore provides high specific surface area, and interface contact between ZnO/dye/electrolyte might be improved.

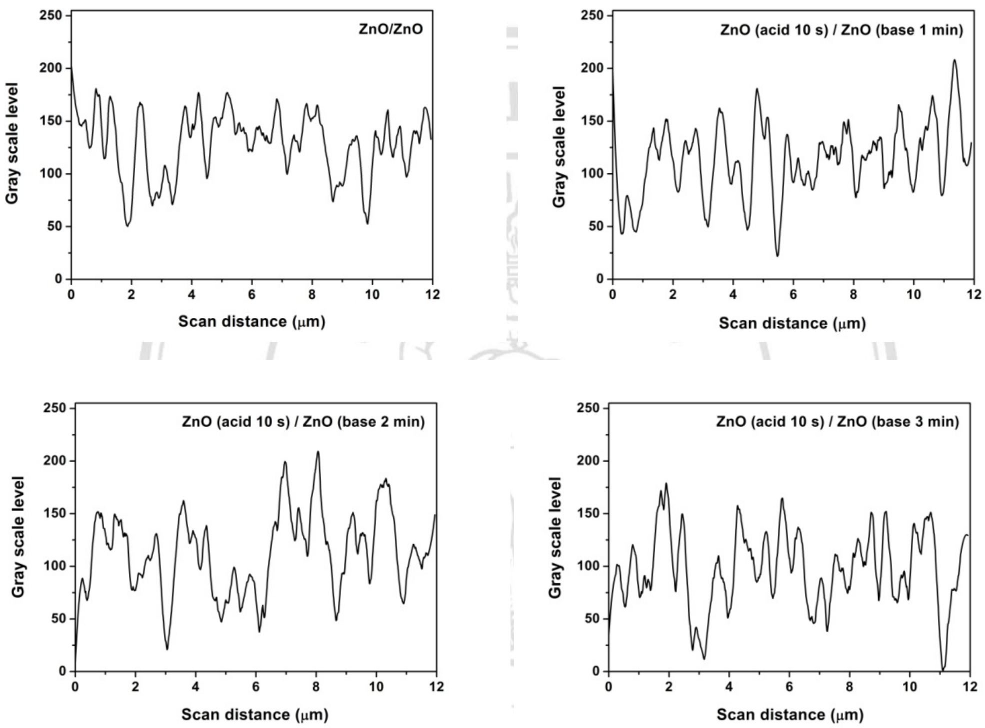

Figure 3.5 Mapping profiles in gray scale level of two-step coating-texturing films.

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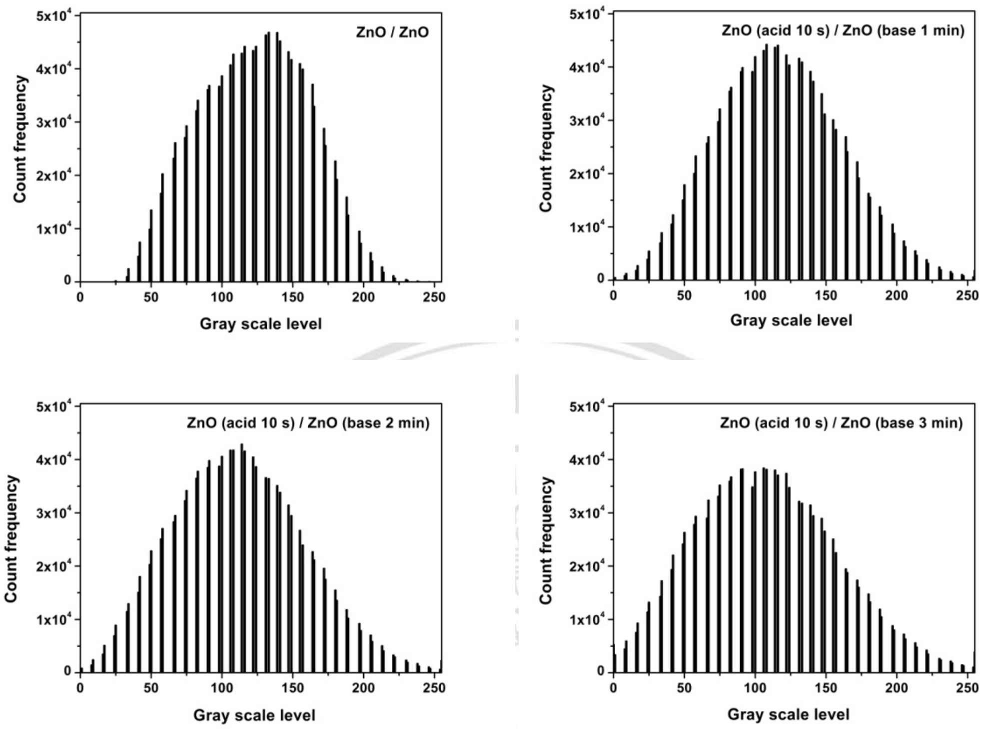

Figure 3.6 Relative pore deep histograms in gray scale level of two-step coating-texturing films.

3.5 Simulated 3D profile analysis

Figure 3.7 shows 3D profiles of the two-step coating-texturing films. It was investigated to better understand of surface pore formation and analyzed surface roughness. The results show a decreased aggregate particles which can be seen a reduction of peak (blue). Meanwhile, pore is formed which can be observed a valley formation (yellow). These results are agreed with both of the mapping profiles and the pore deep histograms. In addition, surface roughness is investigated. The roughness is presented a maximum value of 121.5 nm for ZnO/ZnO films. After the modification, it is found that roughness decreases as increasing texturing time of base solution as seen in Figure 3.8. From the result, it can be described that aggregate particles at surface are faster removed than the deeper particles which resulted in a lower roughness.

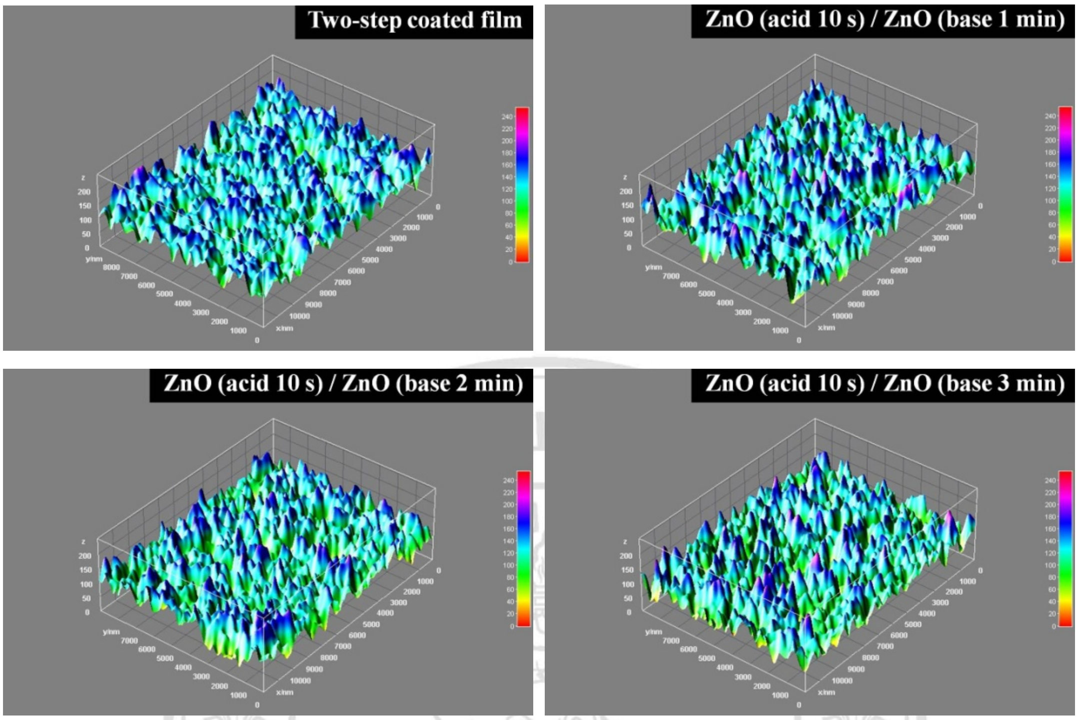

Figure 3.7 Simulated 3D profiles of the two-step coating-texturing films.

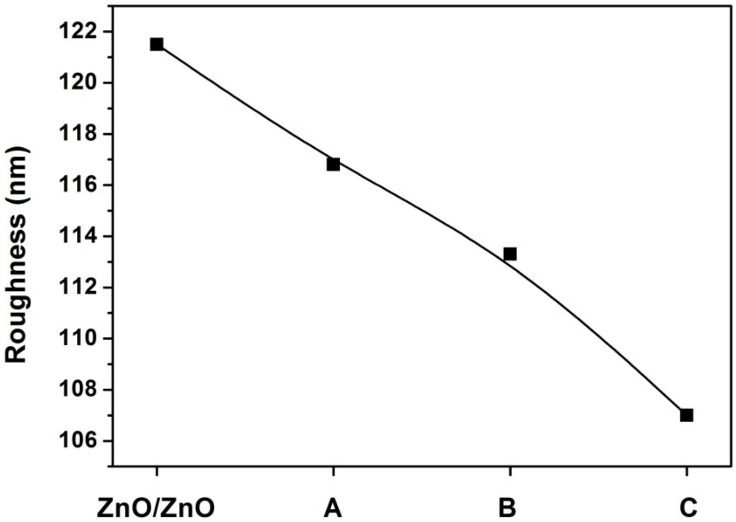

Figure 3.8 Simulated roughness of the two-step coating-texturing films; A, B and C are ZnO(acid 10 s)/ZnO(base 1 min), ZnO(acid 10 s)/ZnO(base 2 min) and ZnO(acid 10 s)/ZnO(base 3 min) films, respectively.

3.6 Photovoltaic characteristics

J-V characteristics curve of fabricated DSSCs is shown in Figure 3.9 and characteristic parameters are summarized in Table 3.2. For DSSCs performance comparison, the DSSCs fabricated with one-step coating films is included. It is found that ZnO/ZnO films exhibit higher J_{sc} and lower FF compare to than ZnO films as expectation. This result confirms an increased dye adsorption and inhibited regeneration process at the ZnO/dye/electrolyte interfaces. After two-step coating-texturing process, J_{sc} is increased for comparing to ZnO films, but it is also decreased in comparison to the ZnO/ZnO films. The decreased J_{sc} represents a lower dye adsorption due to reduced thickness of the films by chemical reaction. However, the J_{sc} is decreased in small values. Moreover, FF is increased after the process indicated that a penetration of electrolyte at the ZnO/dye/electrolyte interface is improved for better regenerating oxidized dye compare to ZnO and ZnO/ZnO films. Therefore, it can be included that the two-step coating-texturing films have potential to solve J_{sc} and FF for DSSCs application as expected.

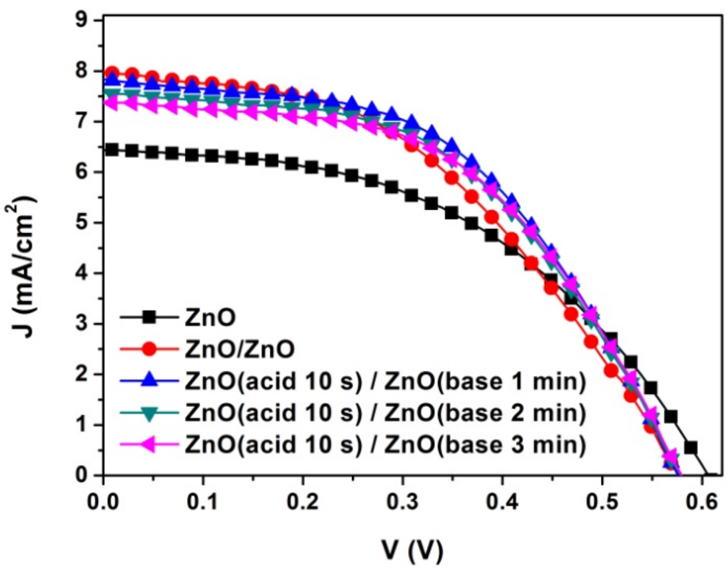

Figure 3.9 Photovoltaic characteristics of DSSCs fabricated with the two-step coating-texturing films. Reproduced with permission from ref [73]. Copyright (2015) Elsevier.

Table 3.2: Photovoltaic parameters of DSSCs fabricated with two-step coating-texturing films.

Films	J_{sc} (mA/cm^2)	V_{oc} (V)	FF	PCE (%)
ZnO	6.43 ± 0.05	0.60 ± 0.01	0.48 ± 0.02	1.85 ± 0.08
ZnO/ZnO	7.98 ± 0.18	0.58 ± 0.01	0.45 ± 0.02	2.06 ± 0.01
ZnO (acid 10 s) / ZnO (base 1 min)	7.84 ± 0.14	0.57 ± 0.01	0.51 ± 0.01	2.28 ± 0.01
ZnO (acid 10 s) / ZnO (base 2 min)	7.57 ± 0.14	0.58 ± 0.01	0.50 ± 0.01	2.20 ± 0.01
ZnO (acid 10 s) / ZnO (base 3 min)	7.39 ± 0.05	0.58 ± 0.01	0.51 ± 0.01	2.21 ± 0.01

3.7 Electrochemical impedance spectroscopy analysis

An electrochemical impedance spectroscopy was measured under dark condition and bias with -0.7 V to investigate recombination process, Nyquist plots and fitting parameters are shown in Figure 3.10 and Table 3.3, respectively. It can be seen that the second semi-circle, which is referred recombination resistance (R_{rec}) at the ZnO/dye/electrolyte interfaces, shows an imperfect semi-circle pattern. It seems a quarter-circle indicating a higher carrier accumulation at the interfaces reflects a higher charge capacity which can be seen in a simulating result in Figure 3.11. The Figure 3.11(a) shows an equivalent circuit for simulation. The R_s, R_{ct1}, R_{ct2} and C_1 are kept constant. The C_2 is varied to 100 μF and 100 μF for investigating a curve pattern. Figure 3.11(b) and 3.11(c) show simulating results with low carrier capacity (represent in term of capacitor, C) and high carrier capacity, respectively. The higher carrier capacity indicates that higher injected electron from excited state of dye molecules is located at the conduction band of ZnO films. This effect might be due to bulk property of thicker ZnO films.

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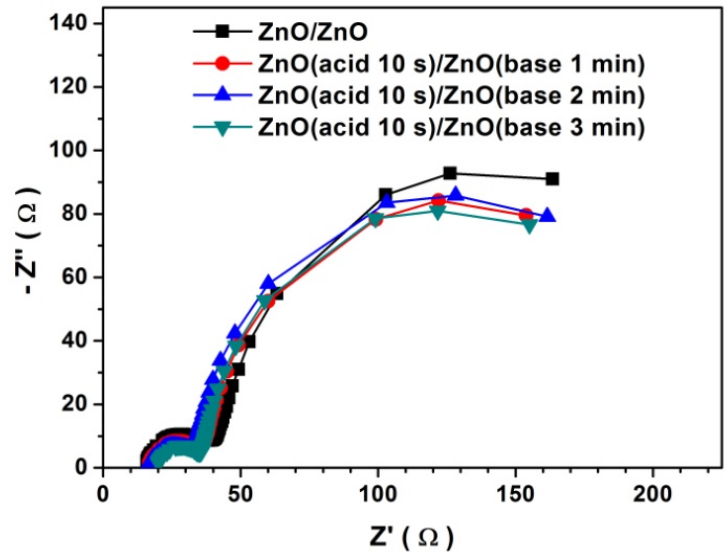

Figure 3.10 Nyquist plots of DSSCs fabricated on the two-step coating-texturing films. Reproduced with permission from ref [73]. Copyright (2015) Elsevier.

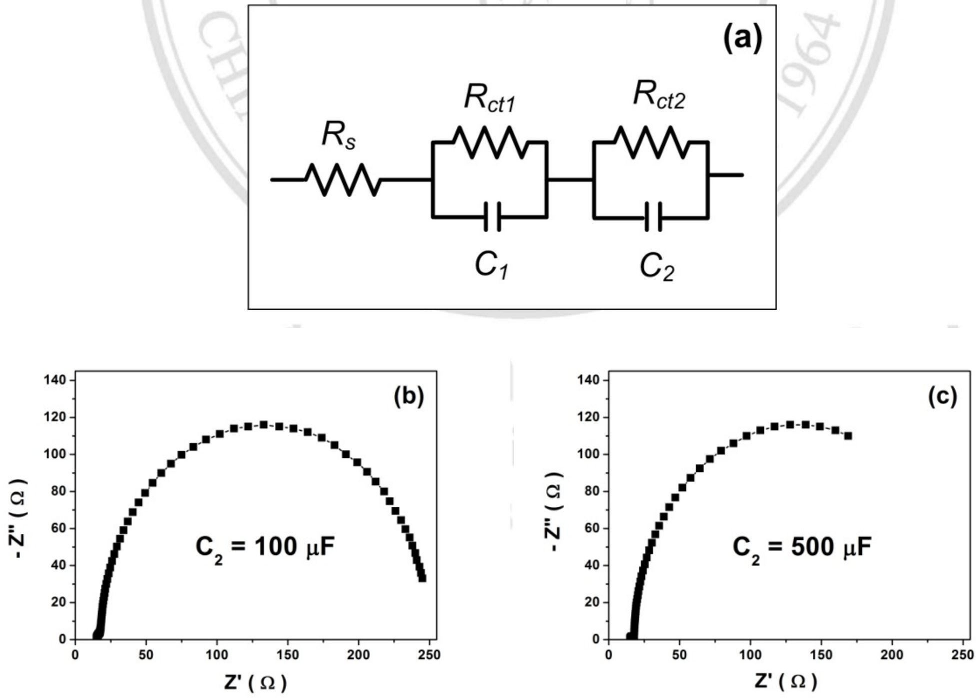

Figure 3.11 Simulating EIS using z-view software; (a) an equivalent circuits, (b) simulated result with low capacitor and (c) simulated result with high capacitor.

From the Table 3.3, the R_{ct2} decreases as increasing the 2^{nd}-texturing time represents a reduced R_{rec} at ZnO/dye/electrolyte interfaces. The result indicates that a recombination of injected electrons from conduction band of ZnO to electrolyte is increased. This effect is a normal occurred due to higher electron charge accumulation at the conduction band [70].

Figure 3.12 shows Bode phase plots of DSSCs, and calculated electron life time was presented in the Table 3.3. It is found that the electron lift time increases for all the films and higher than the ZnO films (see Table 2.4). The increased electron life time is agreed with the higher carrier accumulation at the interfaces result. The longer electron life time refers an increased duration of electron movement at the conduction band of ZnO films before recombines with electrolyte. The result indicates that the injected electrons are in high efficiency of transportation [70].

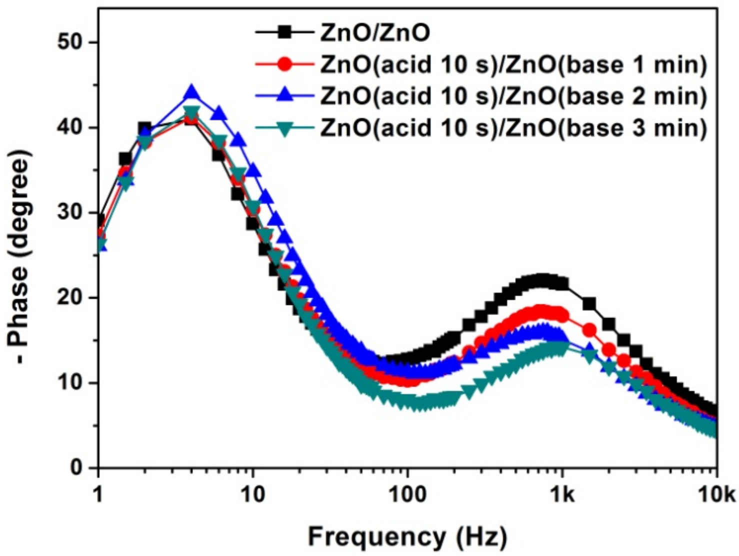

Figure 3.12 Bode phase plots of DSSCs fabricated with the two-step coating-texturing films. Reproduced with permission from ref [73]. Copyright (2015) Elsevier.

Table 3.3: EIS parameters of DSSCs fabricated with two-step coating-texturing films.

Films	**R_s (Ω)**	**R_{ct1} (Ω)**	**R_{ct2} (Ω)**	**f_{peak} (Hz)**	**τ (ms)**
ZnO/ZnO	15.4	26.2	193.9	4	39.8
ZnO (acid 10 s) / ZnO (base 1 min)	16.5	20.4	173.2	4	39.8
ZnO (acid 10 s) / ZnO (base 2 min)	16.4	17.2	178.6	4	39.8
ZnO (acid 10 s) / ZnO (base 3 min)	19.9	16.4	167.3	4	39.8

3.8 Effects of acid solution on photovoltaic performance

A modification of ZnO films by two-step coating-texturing process using an acid solution was investigated to understand acid solution effects on DSSCs performance. The 1^{st}-texturing step was maintained for 10 s and the 2^{nd}-texturing step was varied from 10-30 s. Addition to an investigation of acid texturing effect on each ZnO layers, the films texturing only the 1^{st} or the 2^{nd}-layers represent ZnO(acid 10 s)/ZnO and ZnO/ZnO(acid 10 s), respectively, were included.

Figure 3.13 and Table 3.4 show J-V curve and photovoltaic parameters, respectively. It was found that J_{sc} of texturing films are in between that of ZnO and ZnO/ZnO films, and FF is improved same as the acid-base texturing solutions (see section 3.6). For the only one-layer texturing films, the ZnO(acid 10s)/ZnO shows higher J_{sc} than all of texturing films, but it is in low FF. On the other hand, the ZnO/ZnO(acid 10s) gives high FF but low J_{sc}. An invert change in J_{sc} and FF lead a limitation of PCE enhancement. These effects might be due to an imbalance between thickness and porosity of the films. For the two-step coating-texturing films with acid-acid solutions, a decrease in J_{sc} is observed as increasing the 2^{nd}-texturing time from 10-30 s, but it is in small change. Whereas, the FF is improved compare to the ZnO/ZnO and the one-layer texturing films. Therefore, the PCE is enhanced to be the maximum

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value for the optimized films of ZnO(acid 10s)/ZnO(acid 10s) films. This result implies that an appropriate film was performed by balancing between thickness and porosity. However, effect of thickness was not investigated because the texturing time is very short. Therefore, the thickness was assumed a small change.

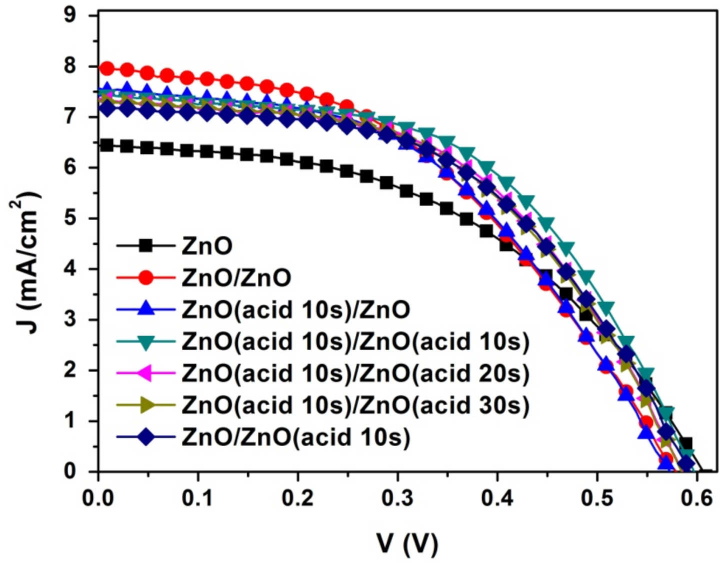

Figure 3.13 Photovoltaic characteristics of DSSCs fabricated with the two-step coating-texturing films using acid solutions.

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Table 3.4: Photovoltaic parameters of DSSCs fabricated with two-step coating-texturing films using acid solution.

Films	J_{sc} (mA/cm^2)	V_{oc} (V)	FF	PCE (%)
ZnO	6.43 ± 0.05	0.60 ± 0.01	0.48 ± 0.02	1.85 ± 0.08
ZnO/ZnO	7.98 ± 0.18	0.58 ± 0.01	0.45 ± 0.02	2.06 ± 0.01
ZnO (acid 10 s) / ZnO	7.56 ± 0.10	0.57 ± 0.01	0.48 ± 0.01	2.06 ± 0.01
ZnO (acid 10 s) / ZnO (acid 10 s)	7.46 ± 0.10	0.59 ± 0.01	0.54 ± 0.01	2.35 ± 0.01
ZnO (acid 10 s) / ZnO (acid 20 s)	7.36 ± 0.06	0.58 ± 0.01	0.53 ± 0.01	2.23 ± 0.01
ZnO (acid 10 s) / ZnO (acid 30 s)	7.33 ± 0.07	0.58 ± 0.01	0.52 ± 0.01	2.18 ± 0.01
ZnO / ZnO (acid 10 s)	7.27 ± 0.08	0.59 ± 0.01	0.52 ± 0.01	2.20 ± 0.01

3.9 Summary of two-step coating-texturing process

Two-step coating (ZnO/ZnO) films based DSSCs show a significant increase in J_{sc} in comparison to the one-step coating (ZnO) films based DSSCs. But it is low in FF due to ZnO particles aggregation which inhibits regeneration process at a ZnO/dye/electrolyte interfaces. After modification using two-step coating-texturing process, a small reduced J_{sc} is observed compare to the two-step coating films. However, PCE is enhanced correlate to an improvement in FF. The result is an effect of porous films formation after the removed aggregate particles caused by chemical corrosion. For the acid-base texturing, the best PCE of 2.28 with FF of 0.51 is obtained for the ZnO(acid 10 s)/ZnO(base 1 min) films based DSSC. Moreover, the acid-acid texturing give the maximum PCE of 2.35% with FF of 0.54 for the ZnO(acid 10 s)/ZnO(acid 10 s) films based DSSC. From the result, it can be conclude that the two-step coating-texturing process demonstrates a successful improvement in J_{sc} and FF.

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The increased J_{sc} is assumed by more dye adsorption due to the increased thickness after two-step coating, and the FF is improved because better interfacial contact of ZnO/dye/electrolyte after two-step texturing. These results lead an enhancement of PCE.

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