

Performances of dye-sensitized solar cell (DSSC) with working electrode of aluminum-doped ZnO nanorods

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ABSTRACT

Renewable energy sources are intensively developed for substituting fossil energy by several routes, such as solar cells and wind power. As a kind of solar cell, dye-sensitized solar cell (DSSC) was studied for low cost and environmentally friendly cell in competing with a silicon-based cell which dominated in the market. But, main problem in DSSC is low current density and power conversion efficiency, especially zinc oxide (ZnO)-based DSSC. In this paper, we enhance the ZnO nanorod properties through the doping of aluminum (Al). For obtaining optimum results, we varied the dopant concentration of 1%, 1.5%, 1%, and 3%. The Al-doped ZnO nanorod was grown by a seed-mediated hydrothermal method at 90°C for 8 hours. The physical properties were analyzed by field emission scanning electron microscopy and EDX, while the photovoltaic properties were analyzed by J-V curve analysis. An improvement of photovoltaic performance up to 200% is obtained by the ZnO nanorod with 1% Al-doped concentration.

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1. INTRODUCTION

Dye-sensitized solar cell (DSSC) is a device capable of converting solar light energy into electrical energy using electrochemical principles. Brian O'regan and Michael Grätzel introduced the DSSC in 1991 which is composed like a sandwich of several main components, namely the working electrode, usually titanium dioxide and zinc oxide, dye, electrolyte as a mediator, and the counter electrode [1]. DSSC is a third-generation solar cell that is promising as an alternative to solar cells because of its advantages, such as low manufacturing costs and a simple process. Gratzel (2004) has succeeded in fabricating this solar cell with an efficiency of about 11% with titanium dioxide (TiO₂) as the active material [2]. However, the price of TiO₂ is more expensive than zinc oxide (ZnO), so the use of ZnO is currently being developed [3].

Some reasons for using ZnO material include an energy bandgap of about 3.3 eV which is similar to TiO₂ of 3.2 eV [4], has high electron mobility, is transparent, has a high transmittance, and is more flexible to be deposited [5]. However, the use of ZnO nanomaterials in DSSC resulted in an efficiency value of 0.27% [6]. This value is still lower for current technology performance., so it still needs to be developed with various treatments and modifications. One of the modification efforts can be done by adding metal atoms through the pending process. ZnO can be doped with group IIIA metal materials, including indium (In), aluminium (Al), gallium (Ga), and boron (B) [7]. Several metal atoms pendants have begun to be carried out on ZnO nanomaterials, including Ga and B [8, 9]. Aluminum doping was chosen because it was cheap, abundant, non-toxic, resistant to corrosion, a good conductor of heat, and electricity [10]. Several types of doping for ZnO synthesis can be in the form of organic compounds containing aluminum metal. The Al metal is used as a dopant atom with

the aim of increasing the electrical conductivity of ZnO [11]. The maximum efficiency of Al-doped that has been achieved is 1.34% [12].

The modification of the ZnO working electrode and the opponent electrode coated with a catalyst material on the DSSC has been widely carried out. In this study, we study the physical properties of ZnO nanomaterials as a working electrode under the addition of Al. The working electrode is a part of the DSSC which donates a large number of electrons in the energy conversion process. The Al metal was chosen because its presence in the active material can improve the electrical conductivity of ZnO [11]. In addition, the choice of Al as a doping agent is also because Al is not easily oxidized and has a distance between atoms that is almost the same as Zn.

2. MATERIALS AND METHODS

2.1. Reagents

Deionized water is used to clean synthesis bottles, substrates, and as a solvent [13]. Zinc acetate dehydrate and zinc nitrate hexahydrate are used as precursors for seed solution in ZnO nanorod plants. Hexamethyltetramine, is used as a surfactant for ZnO nanorod growing solutions. Aluminum (III) nitrate nanohydrate, used as a precursor for doping in ZnO growing solutions. Electrolytes (ionides/triionides), are used as mediators in DSSC.

2.2. Synthesis of ZnO:Al Nanostructure

ZnO nanorod growth also goes through the process of seeding and growing. The seeding process begins with the preparation of the seed solution [14]. The seed solution of ZnO nanorod consists of zinc acetate dihydrate dissolved in 10 ml ethanol with a concentration of 0.01 M. After the seedling solution is ready, the substrate will be placed on a spin coater device, the seed solution will be dropped on the substrate, then the tool is rotated at a fast speed of 3000 rpm for 30 seconds. Then the sample is heated on a hotplate with a temperature of 100°C for 15 minutes, the process will be repeated for 3 repetitions of the seeding, then the sample is annealing in a furnace at 350°C for 1 hour.

The next process after the ZnO nanorod seedling process is the ZnO nanorod growing process. As with the seedling process, the growing process begins with the preparation of a growing solution. The nanorod ZnO growing process begins with the manufacture of a growing solution. The growth solution was made by mixing 0.1 M zinc nitrate hexahydrate, 0.1 M HMT, and 20 ml DI Water then all solutions were sonicated in an ultrasonic bath until the solution was evenly mixed. After all the solutions were evenly mixed, aluminum solution was added with variations in the percentage of Al concentration 0.3%, 1%, 1.5%, 2%, and 3% of the growing solution. The substrate that has been seeded is then put into the growing solution. Then the sample is put in the oven for 3 hours at a temperature of 90°C. When finished, the samples were rinsed using DI Water and dried.

2.3. Characterization and DSSC Performance Test

The characteristics of obtained ZnO nanorod were carried out using FESEM and EDX. DSSC is fabricated by assembling sandwich-formed, which consists of active material (ZnO nanorods with Al-doped), dye N719, electrolytes (iodolyte AN-50) and counter electrodes (plat) with an area active 0.23 cm². The cell performance was tested under artificial sunlight illumination AM 1.5 G, Gamry Framework EPHE 200, with an input power of 100 mW/cm².

3. RESULTS AND DISCUSSIONS

3.1. Nanostructure Morphology

Figure 1 shows the ZnO nanorod that has been doped with Al. Based on the figure, it appears that the ZnO nanorod structure for all variations is hexagonal. The addition of the percentage of Al concentration in ZnO resulted in an increase in the diameter of the ZnO nanorod produced. In addition, the presence of Al in the ZnO nanorod also causes the orientation of the nanorod to look skewed. Giving a 1% Al pending percentage gave ZnO nanorods with smaller diameter, more uniform size, and higher density than the other samples.

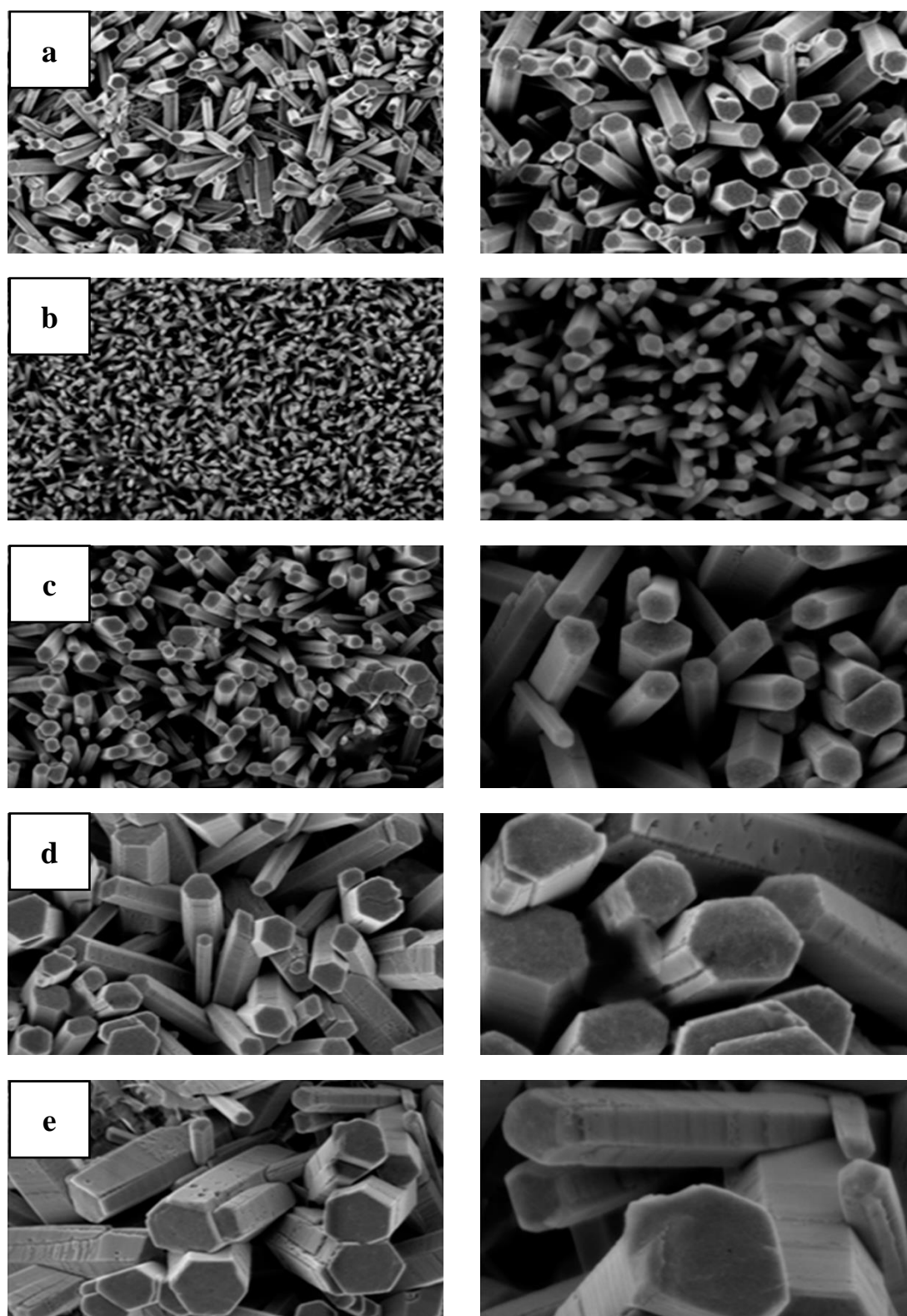


Figure 1. FESEM ZnO:Al photo with a variation of the percentage concentration of: (a) 0.3%; (b) 1%; (c) 1.5%; (d) 2%; and (e) 3% at magnifications of 10,000 times (left) and 30,000 times (right).

3.2. Chemical Composition

The absence of visible Ag or Al particles in the Pt and ZnO nanoparticles made it possible for this pending to enter the Pt and ZnO lattices. To ensure the presence of Ag and Al substituted in the Pt and ZnO lattices, EDX characterization was carried out. EDX spectrum results in Figure 2.

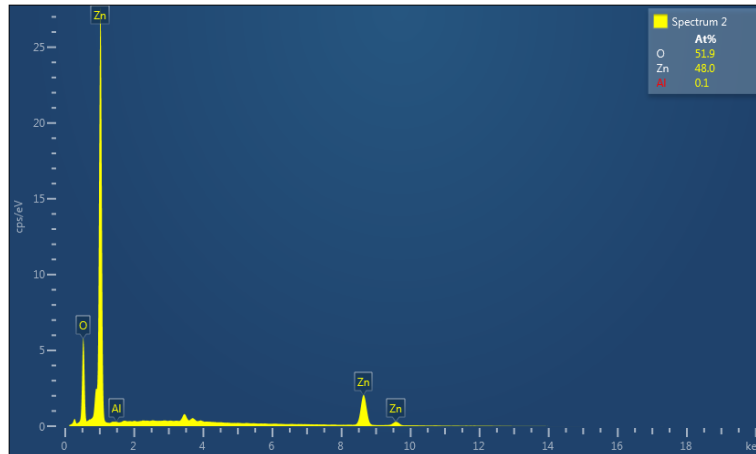


Figure 2. The EDX spectrum of ZnO:Al with a concentration of 1% Al.

Based on the EDX spectrum that has been tested, it is shown the presence of Ag and Al particles in Pt and ZnO. This proves that Ag and Al metals are successfully substituted in the Pt and ZnO nanoparticle lattices. The proportion of atoms of Ag in Pt is 0.2%, respectively 0.2%, 0.1%, and 0% for variations in the concentration of Ag by 1%, 3%, 5%, 7%, and 10%. While the atomic proportion of Al in ZnO is 0.1 for all samples, with variations in the proportion of Al concentration of 0.3%, 1%, 1.5%, 2%, and 3%. From these results, it appears that with this incident, the treatment of the percentage of atomic concentrations that is given means the number of atoms or Al substituted on the Pt and ZnO lattice is getting minimal [15-17]. This has a negative impact on self-achievement.

3.3. Photovoltaic Performances

Based on the J-V plot in Figure 3, the curve provides the same analysis. From cell measurements, it can be seen that, when the cell is not illuminated in general, the curve will form a semiconductor diode characteristic curve pattern on the forward bias so that the curve is in quadrant one or is positive in the presence of a diode typical curve which is the relationship between diode current and voltage between the two ends of the diode [18, 19], while the characteristic curve of the J-V in the illuminated condition, the curve formed is located in the fourth quadrant [20, 21]. When not irradiated, currents arise due to the potential difference from the devices.

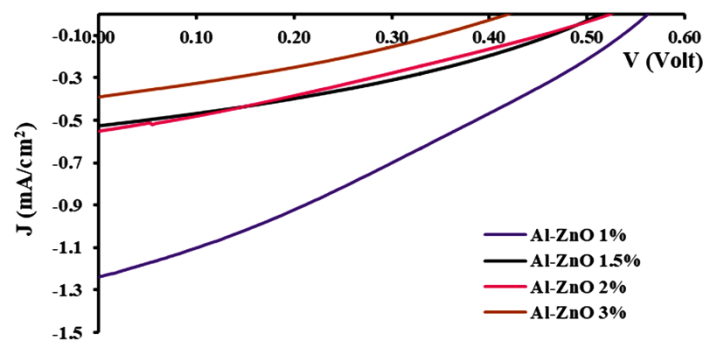


Figure 3. The J-V curve of Al: ZnO under illumination.

When the DSSC device is illuminated by light, there is a response given by the cell to it. This is shown by the current generated by the device. From Figures 3, several physical parameters are obtained that allow the performance of the cell. These results are summarized in Table 1. From the Table 1, it can be seen that the addition of Al and Pt and ZnO increases or increases electron mobility. This is evidenced by the value of J_{sc} , both at Pt:Ag and ZnO:Al. In addition to J_{sc} , the V_{oc} value also increases in both electrodes, the increase in V_{oc} indicates an electron recombination event during the energy conversion process [22, 23]. However, the higher the Ag metal substituted in Pt resulted in a decrease in the J_{sc} and V_{oc} values which had a direct impact on DSSC performance.

Table 1. Physical parameters of the I-V measurement of the cells.

ZnO:Al	V_{oc}	J_{sc}	FF	η (%)
1%	0.561	1.240	0.302	0.210
1.5%	0.513	0.527	0.344	0.093
2%	0.523	0.553	0.290	0.084
3%	0.419	0.391	0.317	0.052

When Ag and Pt are incorporated into the opposing electrode, there are things that must be considered, especially for Pt doped with Ag. Because Ag and Pt are weakening, due to the transfer of electrons when the two materials are reacted [24, 25]. The greater the concentration of Ag given, the weaker the ability of Pt as an electron acceptor at the opposing electrode. This will have a negative impact on cell performance. Meanwhile, the addition of Al to ZnO has a minimum limit of 1%. When the amount of Al concentration is increased, the mobility of the electrons is getting smaller. This is also evidenced from the FESEM and EDX photographs, the increase in the number of concentrations results in an increase in the diameter of the nanorod produced, with a small density. The doped number of Al atoms was also unsubstituted. So that the resulting efficiency value is getting smaller.

4. CONCLUSION

Aluminum doped ZnO nanorods with variations percentage doping concentration of 1%, 1.5%, 2%, and 3% have been successfully grown on FTO using a hydrothermal method with growth temperature of 90°C for 8 hours. FESEM image of the samples shows the diameter of ZnO nanorods ranged from 122.8 nm to 602.9 nm. By 1% Al-doped concentration, the largest surface area and highest are achieved which has a large crystal size and high absorption. Obtained efficiencies of each dopant concentration are 0.210%, 0.093%, 0.084%, and 0.052%, respectively. The improvement effects of Al-doped to ZnO DSSC enable to enhance the efficiency of up to 200% than pristine ZnO.

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REFERENCES

- [1] Ghernaout, D., Boudjemline, A., & Elboughdiri, N. (2020). Electrochemical engineering in the core of the dye-sensitized solar cells (DSSCs). *Open Access Library Journal*, **7**(3), 1–12.
- [2] Alkuam, E., Mohammed, M., & Chen, T. P. (2017). Fabrication of CdS nanorods and nanoparticles with PANI for (DSSCs) dye-sensitized solar cells. *Solar Energy*, **150**, 317–324.
- [3] Iwantono, I., Putri, E. W., Naumar, F. Y., Anggelina, F., Saad, S. K. M., & Umar, A. A. (2016). Performance of dye-sensitized solar cell utilizing Ga-ZnO nanorods: Effect of Ga concentration. *International Journal of Electrochemical Science*, **11**, 7499–7506.
- [4] Kwiatkowski, M., Bezverkhy, I., & Skompska, M. (2015). ZnO nanorods covered with a TiO₂ layer: Simple sol-gel preparation, and optical, photocatalytic and photoelectrochemical properties. *Journal of Materials Chemistry A*, **3**(24), 12748–12760.
- [5] Sharma, V., Kumar, P., Kumar, A., Asokan, K., & Sachdev, K. (2017). High-performance radiation stable ZnO/Ag/ZnO multilayer transparent conductive electrode. *Solar Energy Materials and Solar Cells*, **169**, 122–131.
- [6] Iwantono, I., Nurwidya, W., Lestari, L. R., Naumar, F. Y., Nafisah, S., Umar, A. A., Rahman M. Y. A., & Salleh, M. M. (2015). Effect of growth temperature and time on the ZnO film properties and the performance of dye-sensitized solar cell (DSSC). *Journal of Solid State Electrochemistry*, **19**(4), 1217–1221.
- [7] Dietl, T., Sato, K., Fukushima, T., Bonanni, A., Jamet, M., Barski, A., Kuroda, S., Tanaka, M., Hai, P. N., & Katayama-Yoshida, H. (2015). Spinodal nanodecomposition in semiconductors doped with transition metals. *Reviews of Modern Physics*, **87**(4), 1311–1377.
- [8] Iwantono, I., Tugirin, S., Anggelina, F., Awitdrus, Taer, E., Roza, L., & Umar, A. A. (2016).

- Effect of growth solution concentration on the performance of gallium doped ZnO nanostructures dye sensitized solar cells (DSSCs). *AIP Conference Proceedings*, **1712**(1), 1–8.
- [9] Rahman, M. Y. A., Umar, A. A., Roza, L., Samsuri, S. A. M., Salleh, M. M., Iwantono, I., & Tugirin, T. (2015). Effect of Growth Solution Concentration on the Performance of Boron Doped ZnO Dye-sensitized Solar Cell (DSSC). *Journal of New Materials for Electrochemical Systems*, **18**(4), 213–218.
- [10] Sharmin, A., Tabassum, S., Bashar, M. S., & Mahmood, Z. H. (2019). Depositions and characterization of sol–gel processed Al-doped ZnO (AZO) as transparent conducting oxide (TCO) for solar cell application. *Journal of Theoretical and Applied Physics*, **13**, 123–132.
- [11] Momot, A., Amini, M. N., Reekmans, G., Lamoen, D., Partoens, B., Slocombe, D. R., Elen, K., Adriaensens, P., Hardy, A., & Van Bael, M. K. (2017). A novel explanation for the increased conductivity in annealed Al-doped ZnO: An insight into migration of aluminum and displacement of zinc. *Physical Chemistry Chemical Physics*, **19**(40), 27866–27877.
- [12] Khan, M. A., Magnone, E., & Kang, Y. M. (2016). Elucidation of optoelectronic properties of the sol-gel-grown Al-doped ZnO nanostructures. *Journal of Sol-Gel Science and Technology*, **77**, 642–649.
- [13] Georgiadis, D. E., Tsalbouris, A., Kabir, A., Furton, K. G., & Samanidou, V. (2019). Novel capsule phase microextraction in combination with high performance liquid chromatography with diode array detection for rapid monitoring of sulfonamide drugs in milk. *Journal of Separation Science*, **42**(7), 1440–1450.
- [14] Ghahrizjani, R. T. & Yousefi, M. H. (2017). Effects of three seeding methods on optimization of temperature, concentration and reaction time on optical properties during growth ZnO nanorods. *Superlattices and Microstructures*, **112**, 10–19.
- [15] Jaramillo-Páez, C. A., Navío, J. A., Hidalgo, M. C., & Macías, M. (2018). ZnO and Pt-ZnO photocatalysts: Characterization and photocatalytic activity assessing by means of three substrates. *Catalysis Today*, **313**, 12–19.
- [16] Parra, M. R., Pandey, P., Siddiqui, H., Sudhakar, V., Krishnamoorthy, K., & Haque, F. Z. (2019). Evolution of ZnO nanostructures as hexagonal disk: Implementation as photoanode material and efficiency enhancement in Al:ZnO based dye sensitized solar cells. *Applied Surface Science*, **470**, 1130–1138.
- [17] Mujahid, M. (2015). Synthesis, characterization and electrical properties of visible-light-driven Pt-ZnO/CNT. *Bulletin of Materials Science*, **38**(4), 995–1001.
- [18] Su, M., Zhang, T., Su, J., Wang, Z., Hu, Y., Gao, Y., Gu, H., & Zhang, X. (2019). Homogeneous ZnO nanowire arrays pn junction for blue light-emitting diode applications. *Optics express*, **27**(16), A1207–A1215.
- [19] Manganiello, P., Balato, M., & Vitelli, M. (2015). A survey on mismatching and aging of PV modules: The closed loop. *IEEE Transactions on Industrial Electronics*, **62**(11), 7276–7286.
- [20] Sundqvist, A., Sandberg, O. J., Nyman, M., Smått, J. H., & Österbacka, R. (2016). Origin of the S-shaped JV curve and the light-soaking issue in inverted organic solar cells. *Advanced Energy Materials*, **6**(6), 1502265.
- [21] Cai, X. M., Zheng, Z. W., Long, H., Ying, L. Y., & Zhang, B. P. (2018). Abnormal staircase-like IV curve in InGaN quantum well solar cells. *Applied Physics Letters*, **112**(16).
- [22] Zhao, H., Wu, Q., Hou, J., Cao, H., Jing, Q., Wu, R., & Liu, Z. (2017). Enhanced light harvesting and electron collection in quantum dot sensitized solar cells by TiO₂ passivation on ZnO nanorod arrays. *Science China Materials*, **60**(3), 239–250.
- [23] Elumalai, N. K. & Uddin, A. (2016). Open circuit voltage of organic solar cells: an in-depth review. *Energy and Environmental Science*, **9**(2), 391–410.
- [24] Ning, X., Li, Y., Dong, B., Wang, H., Yu, H., Peng, F., & Yang, Y. (2017). Electron transfer dependent catalysis of Pt on N-doped carbon nanotubes: Effects of synthesis method on metal-support interaction. *Journal of Catalysis*, **348**, 100–109.
- [25] Lin, R., Cai, X., Zeng, H., & Yu, Z. (2018). Stability of high-performance Pt-based catalysts for oxygen reduction reactions. *Advanced Materials*, **30**(17), 1705332.