

MERIT Long-term Overseas Dispatch

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Hosting Institute: Helmholtz Zentrum Berlin, Germany

Period of Stay: October 1, 2022 – December 30, 2022

Research Topic: Charge Carrier Dynamics in Photoelectrodes at Different Timescales

■ Research Content

The purpose of my stay was to elucidate the kinetics of charge carriers in photoelectrode materials at different time scales using time-resolved spectroscopy. Electrocatalyst-modified photoelectrodes are promising systems that directly convert solar energy into chemical energy such as hydrogen. Unfortunately, there are few materials that can utilize visible light, which constitutes the majority of sunlight, and that can transport photoexcited carriers inside the material to surface reactions with 100% efficiency. The reason is the recombination process that occurs during carrier transport. There are variety of



Figure 1. Main gate of Helmholtz Zentrum Berlin

recombination processes such as band-to-band recombination, Shockley-Read-Hall processes, Auger recombination, and surface defect-assisted recombination, which occur on a wide range of time scales from sub-picoseconds to milliseconds. The impact of recombination occurring on these different time scales on photoelectrode performance is still unclear. Therefore, I had an idea to combine three techniques: time-resolved terahertz spectroscopy, which excels in the sub-picosecond to nanosecond time scale; time-resolved microwave conductivity measurement, which excels in the nanosecond to microsecond time scale; and intensity-modulated photocurrent spectroscopy, which can observe the microsecond to millisecond time scale, to quantify the carrier dynamics at each time scale.

There are few research groups that have all three of the above methods in the world. My previous research focused on the surface of photoelectrode materials and developed materials from the chemical aspect. On the other hand, Helmholtz Zentrum Berlin (HZB, **Figure 1**), which I visited this time, specializes in research on physical aspects. I decided to visit HZB not only to learn valuable analytical methods, but also because I wanted to study in an environment where researchers specializing in different research fields work.

During the stay, two types of photoelectrodes, a single crystal and a photoelectrode fabricated by vapor deposition, were prepared for various spectroscopic methods. The single crystal can use almost 100% of the absorbed photons for surface reactions such as Na_2SO_3 oxidation, which is a model reaction, while the vapor-deposited photoelectrode can only demonstrate about 50–60% efficiency. I attempted to clarify the reason for this difference from physical quantities that characterize carrier dynamics, that such as carrier lifetime, mobility, and diffusion length, obtained by spectroscopy. The thickness of the single crystal I had prepared was not suitable for spectroscopy, and in the first half of the project, I struggled to obtain data after repeated attempts and failures. I collected data from intensity-modulated

photocurrent spectroscopy, which was relatively easy to obtain, and repeated discussions with my advisor and Ph.D. students regarding other spectroscopic methods, and eventually completed the experimental plan as originally planned. The analysis is now underway and together with the results of additional experiments, we plan to systematically discuss which time scale carrier recombination is the major issue for improving photoelectrode performance, which has remained unclear. As a future development, I aim to solve the recombination problem by development of novel surface modification, which is my specialty.

■Daily Life in Berlin

Berlin is lined with many tall new buildings. Of course, this is due to the fact that Berlin is the capital of Germany, but it is also due to the fact that the city was severely damaged during the World War II. Many historical legacies remain, including the Berlin Wall (**Figure 2a**), and the Cecilienhof Palace (**Figure 2b**),



Figure 2. (a) Berlin Wall and (b) Cecilienhof Palace in Potsdam

which was used for the Potsdam Declaration. The museums and many World Heritage sites in the area show that life was extremely difficult during the period of division between East and West Germany after the end of the war. The atomic bombing in Japan was also featured prominently.

Public transportation was relatively on schedule. While buses, trains, and trams operated by the BVG were almost always on schedule, high-speed trains operated by DB were frequently delayed. Since the average delay time of the Shinkansen in Japan is said to be about 30 seconds, I realized how great it was and that the happiness we got was not a matter of course. People in the city are very kind. Neighbors in my apartment greeted me with a smile, and staffs on public transportation and in stores were kind and courteous in their responses. It is similar to Japan in that there are a few people who do not speak English. It was a good experience for me to learn a little German as well.

Winter in Berlin was very cold, with a sharp drop in temperature from mid-November and a few snowfalls. I did not check the exact temperature because I felt that I would lose my uncertainty and lose patience if I saw the temperature on the news, but later I heard from a friend that it was about -10 °C. German food was mainly pork, potatoes, and sausages, and I enjoyed traditional dishes at many restaurants. Unfortunately, I did not like them that much and spent the latter half of the trip buying Japanese food at Asian supermarkets and cooking them myself. German beer was very tasty and there was a wide variety, so I enjoyed comparing beers.

My lab colleagues were from numerous countries and regions, including Germany, Netherlands, Turkey, India, Indonesia, and Philippines, and I enjoyed our talk. We were able to talk about a variety of topics over lunch, such as research topics, New Year holidays, home cooking, and popular music. During this stay, I was able to learn about the interesting cultures and characteristics of Germany and other countries, and at the same time, I felt that I was able to rediscover the beauty of Japan.

■Acknowledgements

I would like to thank my supervisor, Professor Kazuhiro Takanabe, my secondary advisor, Professor Takashi Kondo, and the Fellowship for Integrated Materials Science and Carrier Development program for giving me the opportunity to study abroad. I would also like to take this opportunity to thank the HZB staff who kindly agreed to my visit. I am especially grateful to Dr. Fatwa Firdaus Abdi, Deputy Head of Institute for Solar Fuels. My imperfect research plan caused me a lot of trouble, but we had weekly discussions, and as a result, I learned many valuable analytical methods. I would also like to thank Mr. Markus Schleuning, Mr. Erwin Fernandez, and Mr. Sven Schneider, Ph.D. students and postdoctoral fellows, for their daily discussions, guidance in experiments, and for their warm hospitality in listening to my complaints when things did not go well. I would like to express my deepest gratitude to them. Finally, I would like to thank the Japan Society for the Promotion of Science (JSPS) for financial support during my stay in Berlin.