# 論文 / 著書情報
# Article / Book Information

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（博士課程）
Doctoral Program

# 論 文 要 旨

THESIS SUMMARY

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| 系・コース：<br>Department of, Graduate major in | 応用化学<br>応用化学 | 系<br>コース | |
| 学生氏名：<br>Student's Name | ZOU Quan | | |

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| 申請学位（専攻分野）：<br>Academic Degree Requested | 博士<br>Doctor of （ 工学 ） |
| 指導教員（主）：<br>Academic Supervisor(main) | 山元 公寿 |
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要旨（和文 2000 字程度）
Thesis Summary（approx.2000 Japanese Characters ）

Alloy subnanoparticles, as a new class of nanomaterial, have attracted much attention due to their potential for excellent catalysts. The unique properties and application of SNPs remain to be discovered. However, because of the myriad compositions of alloy sub-nanoparticles, it is not easy to study them comprehensively. Recently, AI (Artificial intelligence) technology is permeating into every traditional field. For example, AI chemistry has become a hot topic realizing high-throughput material discovery. The interdisciplinary field of subnano-science and AI may provide vast novel materials that allow providing solutions to various social problems. Based on such conditions, my doctoral research was carried out. This doctoral study marks the beginning of this new area of research.

1. Improvement of electrocatalytic properties by homogeneous alloying of dissimilar elements at subnanoscale

It was found that SNPs can be fully alloyed while phase segregation is easy to occur in NPs. Metals can be categorized into oxyphilic metals and oxyphobic metals. If we combine oxyphilic metals and oxyphobic metals at the subnanoscale, can we find some enhanced catalysts that can never be found at the nanoscale? To address this question, we systematically prepared a series of bimetallic NPs and SNPs(45 combinations). HER(Hydrogen evolution reaction) was chosen as our target reaction considering the simple mechanism. After high throughput screening, we found PtZrOx SNPs were fully alloyed, and PtZrOx NPs were in phase segregated. In addition, PtZrOx SNPs exhibited positive synergy towards HER, while PtZrOx NPs exhibited no synergy towards HER. To test the universality of this phenomenon, we quantify the synergistic effects, HER synergistic effect index(HSI) was put forward by us. Based on the HSI, we found that positive synergistic effects are always available in SNPs, while negative synergistic effects are common in NPs. Moreover, we calculated the bond number of PtZr SNPs by programmed analysis of the STEM video. We found that the Pt-Zr bond played an important role in enhancing HER activity. DFT calculation revealed that $Pt_4Zr_2$ showed the optimal $H_2$ absorbing energy, which qualitatively accounts for the optimal compositional ratio of $Pt_4Zr_2$ SNPs.

2. Revelation of key factors distinguish SNPs and NPs and accelerated discovery of SNPs for HER assisted by machine learning(ML)

On the basis of part1, we acquired a systematic database(45 combinations) of bimetallic SNPs and NPs for HER. However, a further question appeared: why do SNPs always exhibit positive HSI while NPs display the negative HSI? In other words, what are the key factors that distinguish SNPs from NPs? To answer this question, we summarized many important features(atomic number, work function, first ionization energy and etc.) of various elements. We input our database to train the 8 ML algorithms, and it was shown that the work function played a key role in SNPs, while work function and other factors have a synergic effect on the HER activity of NPs. We found the work function is closely correlated with surface structure and compositions. It demonstrated that the fluidity and well-alloyed SNPs could keep a dynamic equilibrium

surface state, which distinguishes the SNPs from NPs. An ANN(artificial neural network) was constructed to improve the prediction accuracy, and the results supported that SNPs are more predictable than NPs, but the results turn out that ANN is powerful but not suitable for this research. Based on this experience and discovery, we successfully built an ML model to predict the HER activity of trimetallic SNPs. It was found that PtPd was the best combination of SNPs for HER.

3. ML assisted revelation of subnanoscale miniaturization induced multifunctionlization and accelerated discovery of multifunctional SNPs

Previous research confirmed that alloying could lead to the multifunctionalization of catalysts. In the first part, we confirmed that subnanoscale miniaturization could lead to the alloying of catalysts. So here comes to next question, can subnanoscale miniaturization lead to the multifunctionalization of catalysts? To solve this question, we intend to apply the SNPs and NPs for ORR (oxygen reduction reaction) and OER (oxygen evolution reaction) to enlarge our database. After the establishment of the database, we categorized the database into 3 groups, bad catalysts, monofunctional catalysts, and multifunctional catalysts, according to the number of reactions they can catalyze. ML learning was applied to classify the SNPs and analyze the key factors in ORR and ORR. It was found that both SNPs and NPs were highly correlated with work function in multifunctional catalyst classification. Moreover, the phenomenon that subnanoscale miniaturization can lead to the multifunctionalization of catalysts was also revealed by the confusion matrix and classification report analysis. Based on these discoveries and the experience of part 2, an ensembled ML model was constructed by us to predict trimetallic SNPs for multi-electron transfer reactions (HER, ORR, and OER). Based on all the ML models, the process of discovery of multifunctional (HER, ORR, and OER) SNPs was greatly accelerated.