Graduate School of Advanced Science and Engineering
Waseda University

博 士 論 文 概 要
Doctoral Thesis Synopsis

論 文 題 目
Thesis Theme

Nanostructured Metal Oxides and Carbides *via* Controlled Thermal Decomposition of Cyano-Bridged Coordination Polymers

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Coordination polymers (CPs), including metal organic frameworks (MOFs) and porous coordination polymers (PCPs), have attracted much attention for years because of their beneficial uses in catalysis, drug-delivery systems, energy, storage, separation, and environmental applications. Recent research efforts have been devoted to tailor-made nanoarchitectured Prussian blue (PB) and its analogues (PBAs), which are important cyano-bridged coordination polymers (CPs) for the aforementioned applications. All of the PB and PBA nanostructures can be simply synthesized by purposefully changing the precursor compositions (*e.g.*, types and concentrations of metal ions, ligands, and chelating agents) and synthetic conditions (*e.g.*, synthetic temperatures, aging temperatures and times, and pHs). The first target of my PhD thesis is the rational design of various PB and PBA nanostructures with uniform shapes and sizes through a solution phase approach. The effect of the synthetic parameters on the final morphology of products is carefully discussed.

Second, a controlled thermal treatment of my PB and PBA nanostructures in air or in an inert atmosphere can yield nanoporous metal oxides and carbides, respectively. The large fraction of metal centers can be utilized as the metal source, and the removable organic components, by simple calcination, can provide nanopores. The original morphology is almost retained, even after the thermal treatments. My strategy has proven to be a promising solid-state method for the preparation of nanoporous metal oxides and carbides with fine crystal structures. This method has great potential to overcome difficulties in the preparation through traditional approaches, such as supramolecular templating. My obtained nanoporous materials show a superior performance as electrode materials for supercapacitors, electrocatalysts for an oxygen reduction reaction (ORR) and oxygen evaluation reaction (OER), and drug carriers for drug delivery systems (DDSs).

Chapter 1 introduces the recent progress related to coordination compounds. Their conversion into functional nanoporous materials is also mentioned.

Chapter 2 explains a thermal decomposition of cyano-bridged Co-Fe CPs with cubic morphology to prepare nanoporous Co-Fe mixed oxides. During the thermal treatment, the organic units (carbon and nitrogen) are completely removed, and only metal contents are retained to prepare nanoporous metal oxides. The original nanocube shapes are retained well even after the thermal treatment. I further extend this concept to prepare nanoporous metal oxides with hollow interiors. Core-shell heterostructures consisting of different metal cyanide hybrid CPs are prepared first. Then, only the cores are dissolved by chemical etching using a hydrochloric acid solution (*i.e.*, the cores are used as sacrificial templates), leading to the formation of hollow interiors in the nanocubes. These hollow nanocubes are also successfully converted to nanoporous metal oxides with hollow interiors by controlled thermal treatment.

In **Chapter 3**, an oriented and controlled crystal growth of various cyano-bridged CPs is realized by using trisodium citrate dihydrate (TSCD) as a chelating agent. After mixing manganese acetate with TSCD, the formed Mn-citrate complex tends to release a few Mn^{2+} ions steadily and slowly, which then react with the ligands at the initial stage of the reaction. Subsequently, the generated nuclei further grow from the interaction

between the released Mn^{2+} and $[Mn(CN)_6]^{3-}$, $[Co(CN)_6]^{3-}$, and $[Ru(CN)_6]^{4-}$ anions to form several types of cyano-bridged coordination polymers (abbreviated as MnCNMn, MnCNCo, and MnCNRu, respectively). After thermal treatment in air, the as-prepared CPs can be decomposed into their corresponding nanoporous Mn-based oxides. Surprisingly, the electrochemical analysis reveals that the Mn-Ru oxide prepared from MnCNRu is a promising catalyst for the production of H_2O_2 by selectively catalyzing the ORR through a 2-electron pathway.

Chapter 4 shows potential applications of PB-derived nanoporous iron oxide. Nanoporous iron oxide nanoparticles with superparamagnetic behavior are successfully synthesized from Prussian blue (PB) cubes through a thermal conversion method and applied to the intracellular drug-delivery systems (DDSs) of bladder cancer cells (*i.e.*, T24) with controlled release and magnetic guiding properties. The synthesized materials show great potential as drug carriers with high biocompatibility, controlled release, and magnetic targeting features for future intracellular DDSs. Furthermore, by tuning the applied calcination temperatures, the crystalline degrees and phases of nanoporous Fe oxides can be controlled from the amorphous phase to the γ-Fe_2O_3 and α-Fe_2O_3 phases. Nanoporous α-Fe_2O_3 with a high surface area is useful for photocatalytic applications.

The two-dimensional (2D) CPs have a highly accessible surface area that permits guest molecules to effectively access the micropores in the CPs. Moreover, 2D CPs have many active sites for catalytic and electrochemical reactions; furthermore, assembled CPs can be used as membrane filters.

Chapter 5 demonstrates a bottom-up synthesis of 2D cyano-bridged Cu-Pt CP flakes using TSCD as a chelating agent, which controls the nucleation and crystal growth. The citrate ions directly interact with Cu ions, as confirmed by a ^1H NMR spectroscopic study. The Cu ions gradually released from the Cu-citrate complex are gradually converted into Cu-Pt CPs in the reaction with $[Pt(CN)_4]^{2-}$. The generation speed of Cu-Pt CPs is significantly delayed in the presence of citrate ions, thereby leading to the controlled growth of single crystalline Cu-Pt CPs with a plate morphology. The lateral sizes of the Cu-Pt CP flakes are controlled by changing the amount of trisodium citrate used. I strongly believe that our method will be useful for the preparation of other types of 2D CP flakes. Such 2D CPs can potentially be used for the preparation of nanoporous metal oxides and carbides with new solid state properties.

Chapter 6 demonstrates the controlled synthesis of cyano-bridged Ni-Ni CPs with 2D morphology. After calcination, the 2D Ni-Ni CPs can be transformed into nanoporous nickel oxide (NiO) with a highly accessible surface area. This strategy is adopted in order to form 2D nanoporous NiO with tunable porosity and crystallinity by changing the applied calcination temperatures. During this thermal treatment, organic units (carbon and nitrogen) are completely removed, and only the metal content remains to take part in the formation of nanoporous NiO. The original 2D flake shapes are almost retained, after thermal treatment at a low temperature, but they are completely destroyed at a high temperature because of further crystallization in the framework. Nanoporous NiO with a high surface area shows significant efficiency and interesting results for supercapacitor application. This concept is also applicable to nanoporous nickel-cobalt mixed oxides. These mixed oxides demonstrate high electrocatalytic activity for an oxygen evolution reaction (OER).

Chapter 7 discusses a novel strategy involving the hybridization of cyano-bridged CP flakes with

graphene oxide (GO) sheets. The positively-charged cyano-bridged Ni-Ni CPs are spontaneously hybridized with the negatively-charged GO sheets and thermally treated in air, so the organic materials can be removed without affecting the integrity of the parent GO sheets. Thus, the layer-by-layer construction followed by a thermal treatment can produce a new hybrid nanoporous material consisting of NiO and GO. The obtained hybrid material exhibits an efficient catalytic activity and stability for the oxygen reduction reaction (ORR). I also demonstrate the *in situ* crystallization of cyano-bridged Ni-Ni CP flakes on the surface of GO sheets. The GO sheets are utilized as a nucleation site, and then the NiCNNi-coated GO sheets self-assemble to form ordered lamellar nanomaterials. This approach might be applied to many other inorganic-organic hybrids for ordered layer-by-layer (LbL) architectures. Thermal treatment under nitrogen yields a Ni_3C-GO composite with a similar morphology to the starting material, and the Ni_3C-GO composite exhibits good electrocatalytic activity and excellent durability in the ORR.

Chapter 8 summarizes this thesis and future prospects. Through this thesis, it is found that the chelating agent strongly affects the speed of the crystallization. With a reaction rate a hundred times slower, the synthetic conditions become optimal to trigger an oriented crystal growth. We have realized various cyano-bridged CP nanostructures with different compositions, which can serve as excellent precursors for the synthesis of many nanoporous metal oxides and carbides. In the future, my strategy can be extended for the synthesis of other tailor-made cyano-bridged CPs with their potential applications for the desired nanoporous inorganic materials.

早稲田大学　博士（工学）　学位申請　研究業績書

(List of research achievements for application of doctorate (Dr. of Engineering), Waseda University)

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種 類 別 (By Type)	題名，発表・発行掲載誌名，発表・発行年月，連名者（申請者含む） (theme, journal name, date & year of publication, name of authors inc. yourself)
○Paper	2D to 3D Self-Construction: One-Pot Coordination-Polymer-Glued Layer-by-Layer Assembly of Graphene Oxide Sheets *Angew. Chem. Int. Ed.* **2016**, *In press*. (11 May, 2016). (DOI: 10.1002/anie.20160322) **Mohamed B. Zakaria**, Cuiling Li, Qingmin Ji, Bo Jiang, Jonathan P. Hill, Katsuhiko Ariga, Yusuke Yamauchi
○Paper	Thermal Conversion of Hollow Prussian Blue Nanoparticles into Nanoporous Iron Oxides with Crystallized Hematite Phase *Eur. J. Inorg. Chem.* **2014**, 1137-1141. (6 February, 2014) **Mohamed B. Zakaria**, Ming Hu, Naoaki Hayashi, Yoshihiro Tsujimoto, Shinsuke Ishihara, Masataka Imura, Norihiro Suzuki, Yu-Yuan Huang, Yoshio Sakka, Katsuhiko Ariga, Kevin C.-W. Wu, Yusuke Yamauchi
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○Paper	Single-Crystal-like Nanoporous Spinel Oxides: A Strategy for Synthesis of Nanoporous Metal Oxides Utilizing Metal-Cyanide Hybrid Coordination Polymers *Chem. Eur. J.* **2014**, 20, 17375 -17384. (30 October, 2014) **Mohamed B. Zakaria,** Hu Ming, Masataka Imura, Rahul R. Salunkhe, Naoto Umezawa, Hicham Hamoudi, Alexei A. Belik, Yusuke Yamauchi
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○Paper	Synthesis of Nanoporous Ni-Co Mixed Oxides by Thermal Decomposition of Metal-Cyanide Coordination Polymers *Chem. Asian J.* **2015**, 10, 1541-1545. (12 May, 2015) **Mohamed B. Zakaria,** Ming Hu, Malay Pramanik, Cuiling Li, Jing Tang, Ali Aldalbahi, Saad M. Alshehri, Victor Malgras, Yusuke Yamauchi

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○Paper	Layer-by-Layer Motif Hybridization: Nanoporous Nickel Oxide Flakes Wrapped into Graphene Oxide Sheets toward Enhanced Oxygen Reduction Reaction *Chem. Commun.* **2015**, 51, 16409-16412. (8 September, 2015) **Mohamed B. Zakaria**, Victor Malgras, Toshiaki Takei, Cuiling Li, Yusuke Yamauchi
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Paper	Fabrication of Asymmetric Supercapacitors Based on Coordination Polymer Derived Nanoporous Materials *Electrochimica. Acta* **2015**, 183, 94-99. (7 May , 2015) Rahul R. Salunkhe, **Mohamed B. Zakaria**, Yuichiro Kamachi, Saad M. Alshehri, Tansir Ahamad, Nagy L. Torad, Shi Xue Dou, Jung Ho Kim, Yusuke Yamauchi

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Presentation	Preparation of Cyano-Bridged Coordination Polymers with Well-Defined Shapes and Their Thermal Conversion into Nanoporous Metal Oxides The 8th International Mesostructured Materials Symposium (IMMS-8), May 20-24, **2013**, Awaji Island, Hyogo, Japan. **Mohamed B. Zakaria**, Ming Hu, and Yusuke Yamauchi
Presentation	Synthesis of Photoactive Nanoporous Hematite Iron Oxide with Hollow Interiors Using Prussian Blue Coordination Polymers The 4th NIMS/MANA-Waseda University International Symposium, March 11th, **2013**, National Institute for Materials Science (NIMS), Sengen-site, Tsukuba, Japan **Mohamed B. Zakaria** and Yusuke Yamauchi
Presentation	Sophisticated Crystallization of Coordination Polymers and Their Thermal Conversion into Nanostructured Metals Oxides The 5th NIMS/MANA-Waseda University International Symposium, March 24th, **2014**, National Institute for Materials Science (NIMS), Sengen-site, Tsukuba, Japan **Mohamed B. Zakaria** and Yusuke Yamauchi
Presentation	Controlled Synthesis of Nanoporous Nickel Oxides with Two-Dimensional Shapes through Thermal Decomposition of Metal-Cyanide Hybrid Coordination Polymers The International Conference of the Nanospace Materials, June 23-25th, **2015**, Department of Chemistry, National Taiwan University, Taipei, Taiwan **Mohamed B. Zakaria** and Yusuke Yamauchi
Presentation	Layer-by-Layer Motif Hybridization: Nanoporous Nickel Oxide Flakes Wrapped into Graphene Oxide Sheets toward Enhanced Oxygen Reduction Reaction MANA-RSC symposium: Materials for Energy Generation and Storage, October 15-16th, **2015**, National Institute for Materials Science (NIMS), Namiki-site, Tsukuba, Japan. **Mohamed B. Zakaria** and Yusuke Yamauchi
Presentation	Controlled Synthesis of Nanoporous Nickel Oxide with Two Dimensional Shapes through Thermal Decomposition of Metal-Cyanide Hybrid Coordination Polymers The 6th Waseda-NIMS International Symposium, July 29th, **2015**, Waseda University, 3-4-1 Okubo, Shinjuku, Tokyo, 169-8555, Japan **Mohamed B. Zakaria** and Yusuke Yamauchi
Presentation	Two Dimensional Pt/CuO-GO Nanocomposites through Thermal Treatment of Cyano-Bridged Coordination Polymer The 6th Waseda-NIMS International Symposium, July 29th, **2015**, Waseda University, 3-4-1 Okubo, Shinjuku, Tokyo, 169-8555, Japan Azhar S. Alowasheeir, **Mohamed B. Zakaria**, Cuiling Li, and Yusuke Yamauchi