### **Grant-in-Aid for Specially Promoted Research**

### **Science and Engineering**



Title of Project: Creation of two-dimensional conjugated polymer, coordination nanosheet, and manifestation of

higher-order functions using high quality and

hetero-structured nanosheets

Hiroshi Nishihara

(The University of Tokyo, Graduate School of Science, Professor)

Research Project Number: 19H05460 Researcher Number: 70156090

Keyword: two-dimensional material, metal complex, crystal, hetero-structure, energy storage

#### [Purpose and Background of the Research]

The coordination nanosheet (CONASH) refers to ultrathin film of a two-dimensional (2D) conjugated polymers composed of metal ions and planar bridging organic  $\pi$ -ligands. We reported the nickelladithiolene (NiDT) CONASH, the first example to show metallic properties, in 2013. Contrarily to inorganic nanosheets such as graphene, CONASH can be synthesized at the liquid-liquid and gas-liquid interface. There are numerous combinations of metals and ligands, such that various chemical structures can be obtained. Also, most coordination reactions proceed under ambient conditions, such that easy and cheap bottom-up synthetic method can be employed. The purpose of this project is to open up new areas of CONASH research in fundamental science and engineering leading to further applications that will contribute to the advancement of our society.

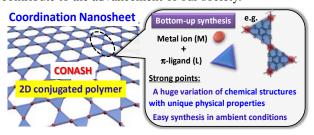


Fig. 1. Concept of CONASH.

#### (Research Methods)

In this research, the following four issues will be tackled; 1) to create new functional CONASHs by combining with a theoretical calculation, 2) to synthesize single crystalline CONASHs of high purity and large area (100 µm<sup>2</sup>) for understanding the essential structure-property correlations, 3) to uncover ultimate physical and chemical functions based on the features of both metal complexes and 2D conjugated structures, and 4) to fabricate hetero-structures (van der Waals-layers and lateral hetero-junction) of CONASHs and discover their unique properties and functions. These issues will be investigated using our past research method and our collaborative research network with physicists and electronic engineers, but a giant leap is necessary in order to synthesize high quality CONASHs. We will achieve this leap by introducing our original new techniques and methods, and will find unprecedented functions and phenomena of CONASH. In particular, we will study on the electrochemical energy storage/conversion functions of CONASH

collaboration with Dr. Ken Sakaushi (NIMS).

## **(Expected Research Achievements and Scientific Significance)**

It has been demonstrated that CONASH is a promising material group utilizable for various applications by the extensive researches since our report of the electronically conducting NiDT CONASH. However, there is still challenge for CONASH to install it in practical applications, *i.e.* a general synthetic approach to prepare high quality nanosheet samples in large scale. One of the aims of this project is to develop a method to obtain the high-quality sample of CONASHs, which directly leads to revealing intrinsic parameters of their physical and chemical properties important for basic science and manifesting high performance important for applications.

Other aims of this project are to design new functional CONASH to investigate ultimate physical and chemical functions, and to fabricate hetero-structures of CONASHs. The progresses of researches on these issues using high quality CONASHs will expand the field of basic and applied research on materials science, chemistry, physics, and electronic engineering etc.

#### [Publications Relevant to the Project]

- π-Conjugated Nickel Bisdithiolene Complex Nanosheet. T. Kambe, R. Sakamoto, K. Hoshiko, K. Takada, M. Miyachi, J. Ryu, S. Sasaki, J. Kim, K. Nakazato, M. Takata, H. Nishihara, *J. Am. Chem. Soc.* **2013**. *135*. 2462-2465.
- Coordination nanosheets (CONASHs): strategies, structures and functions. R. Sakamoto, K. Takada, T. Pal, H. Maeda, T. Kambe, H. Nishihara, *Chem. Commun.* (Feature article) **2017**, *53*, 5781-5801.

**Term of Project** FY2019-2023

**[Budget Allocation]** 418,700 Thousand Yen

# [Homepage Address and Other Contact Information]

http://www.chem.s.u-tokyo.ac.jp/~inorg/nisihara@chem.s.u-tokyo.ac.jp