

論文内容の要旨

論文題目 Architecture of Functional π -Conjugated Coordination Nanosheets of Nickel with Mixed Ligating Groups at Interfaces

(界面を駆使した複数の配位性官能基を持つ機能性 π 共役ニッケル錯体ナノシートの構築)

氏名 Sun Xinsen

孫 欣森

[Introduction]

The unique physical and chemical properties of nanosheets, two-dimensional (2D) materials, such as graphene and transition metal dichalcogenides are of immense research interest. Whereas, the construction of well-defined 2D materials and expansion of their variety remain as challenging research targets. Coordination nanosheets (CONASHs) are 2D materials which can be constructed by bottom-up methods using the complexation reactions of metal ions with organic bridging ligands under ambient conditions. This allows their chemical structures and properties to be precisely tuned and engineered. Our laboratory has exploited various functional coordination nanosheets using interfacial fabrications. However, the diversity of linker ligands has not been extensively explored, resulting in restriction of the available structural motifs.

[Electrofunctional Bis(iminothiolato)nickel and Bis(aminothiolato)nickel Nanosheets]

Since the introduction of the CONASHs based on trinuclear complexes, a type of CONASHs assembled from square-planar metal complexes and aromatic organic moieties, such as dithiolene, aminotriphenylene and diamine, have been extensively studied. Although much efforts have been made to create such kind of 2D coordination polymers, the most of systems prefer to use unitary ligating group to maintain symmetric coordination structures. This severely limits the variation and coordination tunabilities of CONASH. In my research, two π -conjugated nanosheets built from bis(iminothiolato)nickel (NiIT) and bis(aminothiolato)nickel (N2) were synthesized by altering the

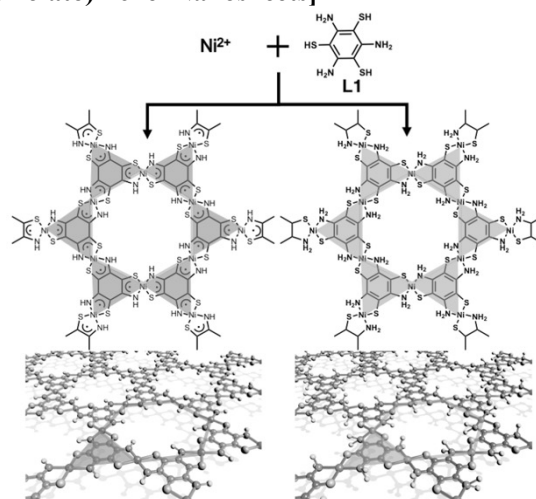


Figure 1. Schematic illustration and chemical structure of monolayer nickel aminothiolene complex nanosheets NiIT and NiAT.

synthetic conditions (Figure 1).

The multilayered sheets were obtained via liquid–liquid interfacial syntheses using an aqueous solution of 1,3,5-triaminobenzene-2,4,6-trithiol (L1) and a dichloromethane solution of bis(2,4-pentanedionato)nickel(II) ($\text{Ni}(\text{acac})_2$). When an oxidant, ferrocenium tetrafluoroborate (FcBF_4), and a base, ammonia, were added to the aqueous layer, a brown flat N1 film was produced (Figure 2a, c). N2 was formed as a lighter yellow nanosheet under the same condition but without the oxidant and the base (Figure 2b, d). The optical microscopy (OM), scanning electron microscopy (SEM), atomic force microscopy (AFM) and transmission electron microscopy (TEM) visualize their uniform sheet-like structure. Thinner **NiIT** and **NiAT** were fabricated using a modified synthetic procedure. Single-layer **NiAT** was produced by a gas–liquid interfacial

reaction via spreading a controlled amount of $\text{Ni}(\text{acac})_2$ onto an aqueous solution of **L1**. Figure 2f shows the single-layer **NiAT** to have a thickness of 0.6 nm. Gas–liquid interfacial synthesis for producing single-layer **N1** was difficult due to the occurrence of rapid aggregation; however, by decreasing the concentrations of **L** and $\text{Ni}(\text{II})$ salt liquid–liquid interfacial synthesis, few-layered **NiIT** 10 nm thick was produced (Figure 2e). I conducted further structural characterization of **NiAT** as it had a better 2D crystallinity due to having larger domains and lower aggregation compared with **NiIT**. Yet, simulation models correlated to this nanosheet system suggest that both **NiIT** and **NiAT** have a hexagonal lattice with similar in-plane unit cell length. Selected-area electron diffraction (SAED) of **NiAT** shows a hexagonal diffraction pattern (Figures 3a), indicating that the sheet has a hexagonal lattice with a unit-cell length of 1.41 nm along the sheet plane (Figures 3b). Grazing incidence X-ray diffraction (GIXD) analysis of **NiAT** found prominent peaks which match the diffraction pattern of the staggered stacking structure (Figures 3c). GIXD also confirmed the hexagonal lattice and in-

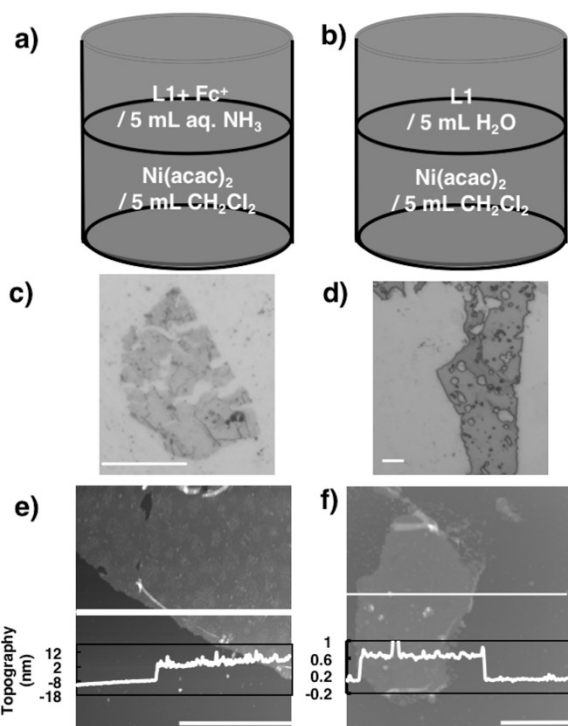


Figure 2. Schematics of the liquid–liquid interfacial synthesis of multi-layer **a**, **NiIT** and **b**, **NiAT**. Optical microscopic images of multi-layer **c**, **NiIT** and **d**, **NiAT**. Scale bars represent 20 μm for both images. **e**, AFM image of few-layered **NiIT**. Scale bar, 5 μm . **f**, AFM image of single-layer **NiAT** and its cross-section analysis along the magenta line. Scale bar represents 3 μm .

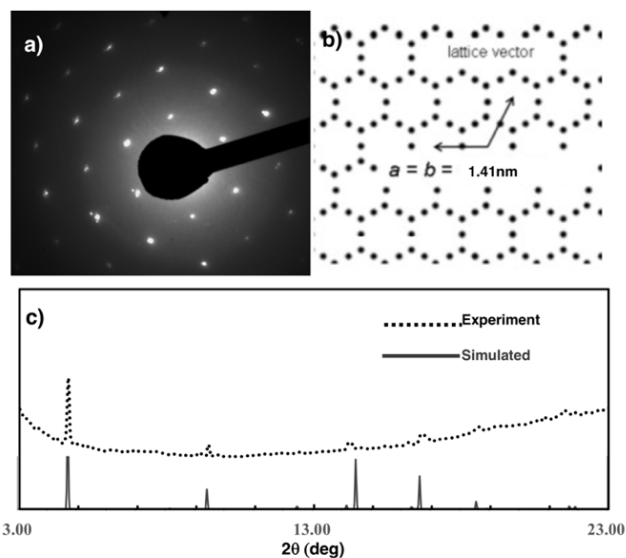


Figure 3. **a**, SAED pattern of **N2**. **d**, Hexagonal two-dimensional lattice that gives the SAED pattern. **c**, Experimental and simulated GIXD patterns of **N2**.

plane lattice constants found by SAED and indicated a interlayer distance of 0.42 nm.

NiIT and **NiAT** were further characterized and differentiated by X-ray photoelectron spectroscopy (XPS) and IR spectroscopy. The XPS revealed that both **NiIT** and **NiAT** with targeted elemental ratios, while both are electrically neutral (Figures 4a-c). The distinct peak shapes and positions in the N–H stretching region of IR spectra reveal the imino structure of the

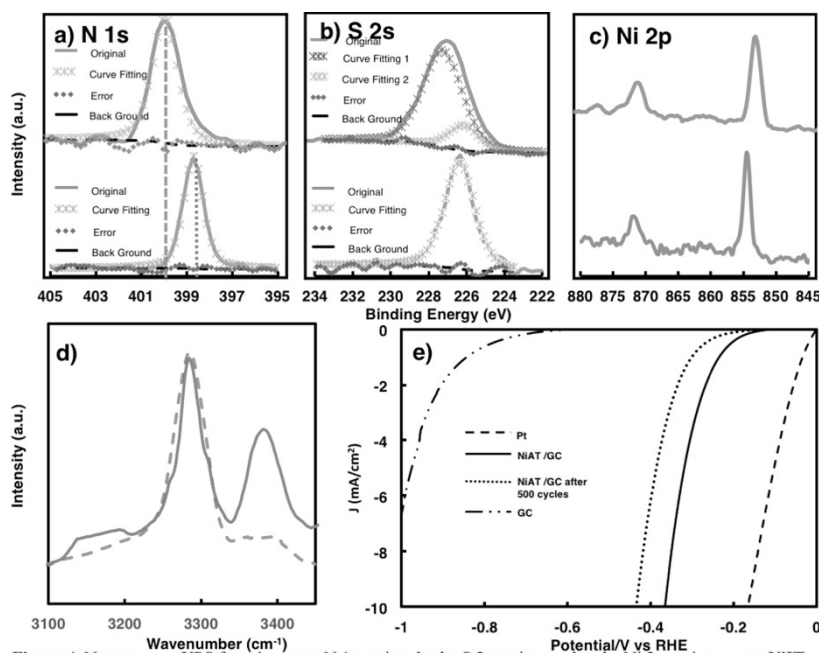


Figure 4. Narrow-scan XPS focusing on **a**, N 1s region, **b**, the S 2s region, and **c**, the Ni 2p region. upper **NiIT** bottom **NiAT**. **d**, IR of the N–H stretching vibration region of **NiIT** (dash) and **NiAT** (solid). **e**, HER of **NiAT**.

ligand of **NiIT** while **NiAT** possesses a pristine amino group (Figures 4d), corroborating the XPS results.

Moreover, this system showed an interesting chemical redox interconversion. **NiAT** can be oxidized to **NiIT**, and then restored back to **NiAT** by chemical reduction. This was confirmed directly by monitoring the characteristic IR N–H stretching signals. This interconvertible phenomenon is also reported on correlated mononuclear complexes (A. Das *et al.*, *ACS Catal.* **2015**, *5*, 1397-1406), which showed promising adaptability of coordination properties to well-defined two-dimensional materials. Furthermore, **NiIT** showed an electrical conductivity of $1 \times 10^{-1} \text{ S cm}^{-1}$ with semiconductive nature of the activation energy of 41 meV, while **NiAT** suggest it to be close to an insulator with the activation energy of 113 meV and the conductivity of $3 \times 10^{-6} \text{ S cm}^{-1}$ at room temperature. This large change in conductivity is rationalized by the difference of band structures between **N1** and **N2**. Considering the interconvertibility of this system, π -conjugated nanosheets **NiIT** and **NiAT** could lead to promising applications in molecular electronics and materials.

Finally, semiconducting nano-sheet **NiAT** on glassy carbon (GC) was subjected as an electrocatalyst for the hydrogen evolution reaction (HER) in acidic aqueous solutions. At pH = 1.3, the onset potential for hydrogen evolution for **NiAT** was -0.15 V vs reversible hydrogen electrode (RHE) (Figures 4e), which is one of the highest among immobilized catalysts for the HER. Moreover, the XPS of **NiIT** remained constant regarding components ratios and valence state after 500 HER cycles, demonstrating high acidic and electrochemical durability.

[Bis(iminophenolato)nickel Nanosheet]

The mixed ligating groups protocol was then applied to the synthesis of another CONASH comprising bis(iminophenolato)nickel core. Instead of thiol group, hydroxyl containing complex may often inhabit higher

crystallinity, due to avoiding the “softness” (charge variance) of sulfur. Therefore, this system may contribute as a pathfinder for further tuning sheet fabrication techniques and morphology analyzation. Multiple biphasic systems composed of an aqueous solution of the triaminotriolbenzene (**L2**) and an organic solution Ni(II) salt afforded bis(iminophenolato) nickel nanosheet (**NiIP**) at the interface (Figure 5a). The as-prepared **NiIP** was transferred onto a substrate using Langmuir-Schäfer method.

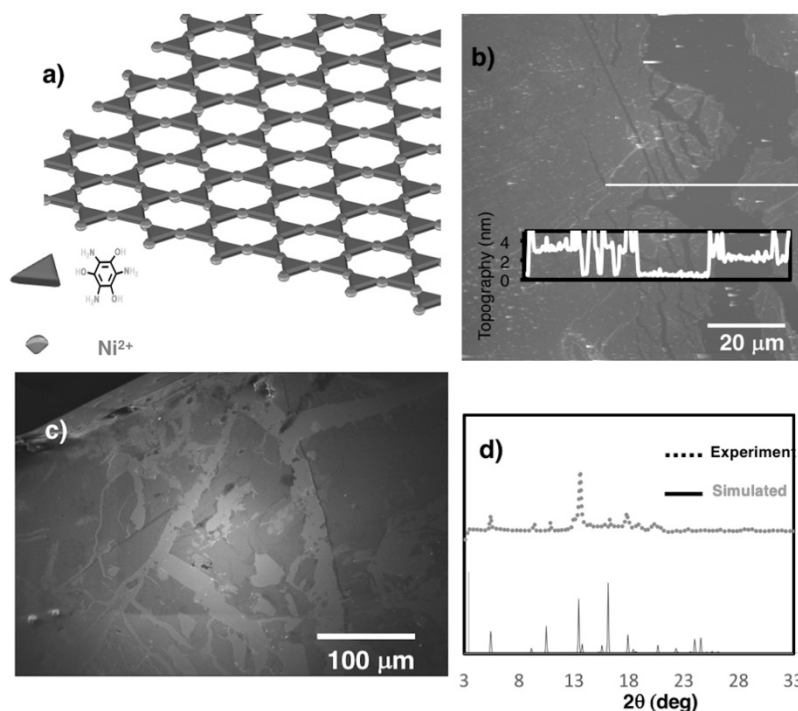


Figure 5. a, Schematic illustration and chemical structure of monolayer nickel iminoiol complex nanosheets **NiIP**. b, AFM of **N3**. c, SEM of **N3**. d, PXRD of **NiIP**.

Microscopic analyses display that the nanosheet exhibits uniform film morphology, as well as an extraordinary large domain size with a few-layered thickness of 2 nm (Figure 5b). The domain size of **NiIP** could be further enlarged using a modified synthetic approach, a gas/liquid interfacial synthesis with Langmuir–Blodgett method. SEM visualize its sheet-like morphology with over 100 μm domain. Powder X-ray diffraction features several peaks, deriving a hexagonal lattice with an in-plane unit cell length of 1.32 nm and inter-layer distance of 0.48nm.

[Conclusion]

In this series of research, a variety of CONASHs composed of mixed functional group linker were synthesized via multiple interfacial systems. Remarkably, by inhabit traditional coordination chemistry into 2D material, the CONASHs can be tailored for various properties, which could lead to promising applications in molecular electronics and materials and considerably affect the practical utility of this type of 2D nanomaterials.