

DOCTORAL THESIS

Synthesis, characterization and applications of bottom-up metal complex nanosheets

Liu, Yurong

Date of Award:
2018

[Link to publication](#)

General rights

Copyright and intellectual property rights for the publications made accessible in HKBU Scholars are retained by the authors and/or other copyright owners. In addition to the restrictions prescribed by the Copyright Ordinance of Hong Kong, all users and readers must also observe the following terms of use:

- Users may download and print one copy of any publication from HKBU Scholars for the purpose of private study or research
- Users cannot further distribute the material or use it for any profit-making activity or commercial gain
- To share publications in HKBU Scholars with others, users are welcome to freely distribute the permanent URL assigned to the publication

Abstract

Inspired by the successful insulation of graphene and declaration of band gap transition in single-layer molybdenum disulfide, low-dimensional materials, possessing unique physical and chemical properties, represent a spotlight in recent years. To extend the promising ultrathin architectures, a series of terpyridine-based ligands as well as multi-hydroxy based ligand, which are all aromatic and offer several desirable features for supramolecular coordination chemistry, were synthesized. A bottom-up approach, namely, liquid-liquid interfacial reactions between organic ligands and cobalt(II) metal ion were employed to assemble the corresponding terpyridine-based cobalt(II) complex nanosheets with different topological constructions, pore sizes and tailor-made functionalities. Also, the approach was applied to the three-way hydroxy derivative and copper(II) ion to generate the π -conjugated copper(II) complex coordination nanosheet. Various chemical and physical analysis techniques, such as electron microscope analysis, elemental analysis, energy level analysis and electrochemical analysis, were carried out to put a detailed insight into the individual networks. Then, the terpyridine based sheets were used as electrodes in the battery system to show their potential application in energy storage.

At the beginning, a brief overview of two-dimensional materials as well as an introduction of the organic metal complex nanosheets was presented in chapter 1.

In this section, the attention was mainly focused on the concept of the 2D nanomaterial, including the design strategies, the categories, the synthetic approaches and the characterization methods. Also, the materials used as electrodes of batteries for energy storage were generally introduced. Those electroactive materials were classified according to their different functional mechanism. The opportunity and challenge of this kind of electroactive materials were then demonstrated. At last, the current development of the 2D materials as electrodes, including the typical structures and the superiority, was indicated.

In chapter 2, two organic metal complexes nanosheets **1-Co** and **2-Co** were prepared by combination of the trifunctional terpyridine based ligands (**L1** and **L2**) and cobalt(II) ions, respectively. Those two terpyridine based triphenylamine derivatives featured the electron rich centers compared with the other benzene centered nanosheets presented in the next chapter. We studied the nanosheets, which possess topologically structurally repeated hexagonal unit, by the above-mentioned analysis methods. The two nanosheets were both colored transparent films. But when they underwent an electrochemical process, they could change the color, showing the electrochromic behavior. The color of **1-Co** was switched from red to green while that of **2-Co** was changed from slight red to orange when a positive voltage was applied to the three-electrode system, in which the nanosheet modified ITO was used as a working electrode. Further electrochemical measurements were conducted to study the electrical response of the nanosheets.

Then the fabricated simple devices, which were constructed with nanosheet supported ITO, conductive polymer film and blank ITO in a sandwich configuration, also showed the reversible electrochromism.

In chapter 3, a series of three-way terpyridine substituted, benzene-based ligands (**L3**, **L4**, **L5**, and **L6**) were coordinated with cobalt(II) ions, resulting in the corresponding nanosheets (**3-Co**, **4-Co**, **5-Co** and **6-Co**) with topologically hexagonal grids. As in chapter 2, structural characteristics were studied through various technologies. Then the focused electroactivity was investigated. Structurally speaking, the difference among these trifunctional ligands is the spacer length from the center to the functional coordination group. And with the increase of the arm-length, the created nanosheets displayed diverse properties. For example, **3-Co** could be applied as the electroresponsive medium together the Au nanoparticle to show the limited surface plasmon resonance switching behavior while **5-Co** with longer arm-length failed to show this phenomenon. In addition, compared with **1-Co** and **2-Co**, **6-Co** displayed an irreversible electrochromism under a positive voltage scan. The distinction of their behavior indicated that the tunability in properties as well as in applications could be achieved by the elaborated structural design. The selected nanosheet **4-Co** was also employed to assemble an electrode of a battery.

A brand-new symmetric four-way terpyridine derivative (1,2,4,5-tetrakis(4-(2,2':6',2''-terpyridyl)phenyl)benzene) (**L7**) was then designed and coordinated

with Co(II) ion to assemble a novel bottom-up multilayer nanosheet **7-Co** in chapter 4. The generated nanosheet featured moderate mechanical strength and insolubility in both aqueous solution and organic solvent, which can facilitate the purification and collection of the product. By taking the advantages of the reversible and robust redox activity of $\text{Co}^{2+}/\text{Co}^{3+}$, a dual-ion battery cathode was achieved by employing the **7-Co** and thus it reveals the possibility of this kind of metal organic complex nanosheet to be utilized in a battery.

In chapter 5, the formed coordination nanosheet **8-Cu** featured π -conjugated metal organic complex motif. The complex unit was not only a connector, but also could function as an active site. The interface-assisted synthesis provided a simple and low-cost method to produce this kind of nanosheet with flat morphology and uniform composition, which was confirmed by several physical and chemical characterization techniques. It expanded the availability of the liquid-liquid interface assisted method to different nanosheets with different metal type or ligand structure.

Finally, the findings, analysis results and future work were concluded in chapter 6. And the experimental details were described in chapter 7.

Table of Contents

DECLARATION.....	i
Abstract.....	ii
Acknowledgements.....	vi
Table of Contents.....	viii
List of Tables	xiv
List of Figures.....	xv
List of Schemes	xxxiii
List of Abbreviations and Symbols	xxxv
Formula Index	xxxix
Chapter 1 Introduction	1
1.1 Background.....	1
1.2 Two-Dimensional Materials	4
1.2.1 Classification of Two-Dimensional Materials.....	7
1.2.2 Approaches to Two-Dimensional Materials.....	10
1.2.3 Analytical Characterization.....	15
1.2.4 Bottom-up Metal-Organic Complex Nanosheets.....	16
1.3 Electroactive Materials Used in Battery Systems.....	20

1.3.1	The Composition and Mechanism of a Battery System	21
1.3.2	The Materials as Electrodes of Battery Systems	25
1.3.3	Two-Dimensional Nanosheets as Battery Electrodes.....	28
1.4	Scope of This Thesis	33
	References	36
Chapter 2 Bis(terpyridine) Cobalt(II) Complex Nanosheets Based on		
Triphenylamine Derivatives		
		51
2.1	Introduction.....	51
2.2	Synthesis of Ligands.....	54
2.3	Synthesis of Cobalt Complex Nanosheets	56
2.4	Characterization of Cobalt Complex Nanosheets	64
2.4.1	Morphology of Nanosheets	64
2.4.2	Chemical Elemental Analysis.....	73
2.4.3	Other Characteristic Measurements	82
2.5	Properties and Application of Cobalt Complex Nanosheets.....	85
2.5.1	The Electrochemical Properties.....	86
2.5.2	The Application of Nanosheets	96
2.6	Conclusion	97
	References	99

Chapter 3	Bis(terpyridine) Cobalt(II) Complex Nanosheets Based on Tri-Substituted Benzene Ligands	104
3.1	Introduction.....	104
3.2	Synthesis of Ligands.....	105
3.3	Synthesis of Cobalt Complex Nanosheets	109
3.4	Characterization of Cobalt Complex Nanosheets	114
3.4.1	Morphology of Nanosheets	114
3.4.2	Chemical Elemental Analysis.....	127
3.4.3	Other Characteristic Measurements	137
3.5	Properties and Application of Cobalt Complex Nanosheets.....	140
3.5.1	The Electrochemical Properties of 3-Co and 5-Co	140
3.5.2	The Electrochemical Properties and Application of 4-Co	148
3.5.3	The Electrochemical Properties of 6-Co	150
3.6	Conclusion	153
	References	155
Chapter 4	Bis(terpyridine) Cobalt(II) Complex Nanosheets Based on Tetrakis-(terpyridine) Ligand.....	157
4.1	Introduction.....	157
4.2	Synthesis of Ligand	160

4.3	Synthesis of Cobalt Complex Nanosheet.....	161
4.4	Characterization of Cobalt Complex Nanosheet	167
4.4.1	Morphology of Nanosheet.....	168
4.4.2	Chemical Elemental Analysis.....	181
4.4.3	Other Characteristic Measurements	187
4.5	Application of Cobalt Complex Nanosheet.....	191
4.6	Conclusion	195
	References	197
Chapter 5	π -Conjugated Bis(hydroxy) Copper(II) Complex Nanosheets.....	203
5.1	Introduction.....	203
5.2	Synthesis of Copper Complex Nanosheet	204
5.3	Characterization Copper Complex Nanosheet.....	207
5.3.1	Morphology of Nanosheet.....	207
5.3.2	Chemical Elemental Analysis.....	210
5.4	Conclusion	213
	References	215
Chapter 6	Conclusion and Future Work.....	218
Chapter 7	Experimental Details	220

7.1	General Procedures	220
7.1.1	Materials	220
7.1.2	Apparatus.....	221
7.1.3	Pretreatment of Substrates	223
7.1.4	Transfer of the Nanosheets to Substrates	223
7.2	Synthetic Procedures of Ligands	224
7.2.1	Synthesis of L1	224
7.2.2	Synthesis of L2	229
7.2.3	Synthesis of L3	232
7.2.4	Synthesis of L4	236
7.2.5	Synthesis of L5	239
7.2.6	Synthesis of L6	245
7.2.7	Synthesis of L7	249
7.3	Synthesis of Nanosheets and Referential Complex R	254
7.3.1	General Procedures of Nanosheet Synthesis	254
7.3.2	Synthesis of Nanosheets and Small Molecule R	254
7.3.3	Thickness Control of Nanosheets	259
	References	265

List of Publications..... 266

CURRICULUM VITAE..... 267