DOCTORAL THESIS

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

Liu, Yurong

Date of Award:
2018

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 $Co^{2+/}Co^{3+}$, 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.

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