

論文の内容の要旨

Study on Two-dimensional π -Conjugated Pd and Pt Dithiolene Polymers

(パラジウムおよび白金の二次元 π 共役ジチオレン錯体ポリマーの研究)

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Introduction

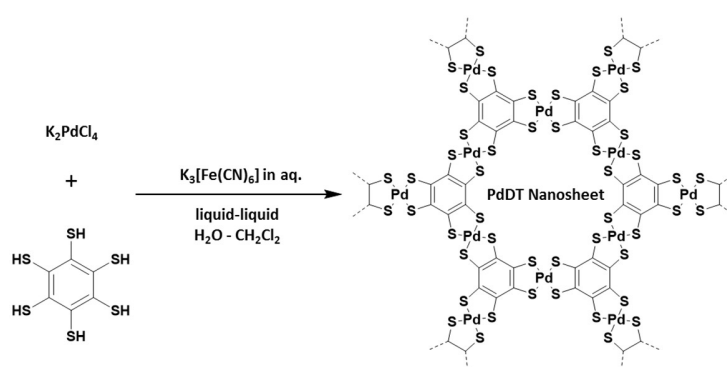
After establishment of quantum confinement, lower order of dimensionality progressed much of its course; two-dimensional (2D) materials gained significant attention in the fields of material science and nanoscience due to their varied properties such as spintronic, ferroelectric, thermoelectric, optoelectric, and electrochromic characteristics. The top-down approach have saturated the scope of use of the elements of the periodic table. Using bottom-up fabrication and coordination chemistry, 2D sheets are synthesized and their properties can be tuned by a variety of metals and significant ligand design. Dithiols, an important class of non-innocent ligand system owing to their interesting electronic structure, have interested researchers to focus on their multi-nucleated 2D coordination nanosheets.

Previously in our laboratory, π -conjugated bis(dithiolato)nickel nanosheet was prepared and it was found that interesting electronically conductive behavior is a function of its electronic states. Later, Liu et al. predicted that the nanosheet can be an organic 2D topological insulator by theoretically calculation. In reference to topological insulators, the spin orbit coupling (SOC) is strong enough to invert the insulating energy gap via surface states. In my Ph.D research, I focus at investigating on the synthetic strategies, electronic states and conductive behavior of heavier group 10 (Pd and Pt) metalladithiolene nanosheets due to the fact that heavier atoms have higher SOC. It should be noted that their synthesis is challenging because the method to synthesize nickelladithiolene nanosheet by the reaction of Ni(II) ions and benzenhexathiols (BHT) cannot be simply applied because Pd(II)

and Pt(II) ions are easy to be reduced by thiols to produce metals. I established novel synthetic methods of Pd and Pt dithiolene nanosheets.

Fabrication and Identification of Palladium dithiolene(PdDT) Nanosheet

A liquid–liquid interfacial reaction of K_2PdCl_4 and NaBr in an aqueous phase with benzenehexathiol in an organic phase (dichloromethane) were performed. After leaving the two-phase solution to stand overnight, a thin lustrous black film with 2–3 μm thickness was formed at the interphase (the product is referred as PdDT'). TEM measurements and powder XRD revealed a layered structure



Scheme 1. Synthetic strategy for preparation of PdDT

containing palladium nanoparticles PdNPs with a diameter of 3–5 nm as shown in Figure 1a. This implies that non-innocent BHT reduced Pd^{2+} to Pd^0 . $K_3[Fe(CN)_6]$ was added as a redox buffer before the second layering of the aqueous Pd^{2+} solution as shown in Scheme 1. The amount of $K_3[Fe(CN)_6]$ strongly affected the film formation and was optimized (referred as PdDT). TEM analysis demonstrated a sheet-like structure without PdNPs (Figure 1b). SAED results gave diffraction points (Figure 1c), which demonstrate a hexagonal structure.

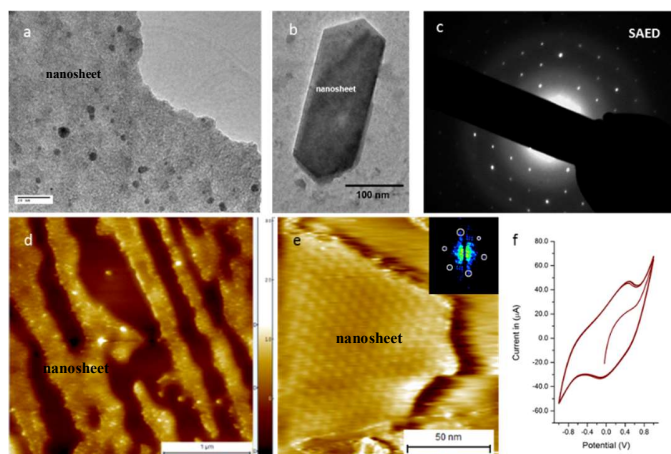


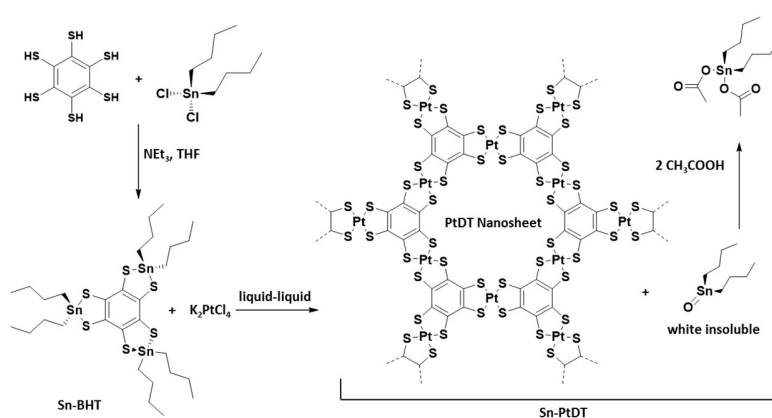
Figure 1. a. TEM image showing nanosheet containing PdNPs, b. nanosheet without PdNPs, c. SAED of b showing hexagonal pattern, d. AFM topography image for 2.5 μm , e. STM image for single layered PdDT, f. CV for PdDT.

The synthesis of ultrathin PdDT sheets with atomic thicknesses was attempted using the gas-liquid interfacial reaction method. An ethyl acetate solution of BHT was sparged on an aqueous solution of K_2PdCl_4 . AFM was exploited to determine the thickness of few layered nanosheets of 4–10 nm (Figure 1d). Using STM analysis, I observed hexagonal patterns (Figure 1e) assigned as a moiré pattern by the superimposition of two lattices: one is in-plane nanosheet and the other is derived from HOPG.

On the other hand, X-ray photoelectron spectroscopy (XPS) analysis revealed the existence of each element (C, S, Pd, K) and the mixed valent oxidation state of $[\text{PdS}_4]^n$ ($n = 0, -1$). Additionally, a reversible redox wave based on ligand center on highly ordered pyrolytic graphite (HOPG) was observed, which again suggest to possess the mixed-valence state of 0 and -1. The electrical conductivity of the samples measured by the standard four-probe method for a pelleted thin film of PdDT' was in order of 10^{-2} Scm^{-1} at 298 K, whereas a pelleted PdDT film also showed a value of the same order.

Fabrication and Identification of the Platinum Dithiolene (PtDT) Nanosheet

A liquid–liquid interfacial reaction of K_2PtCl_4 and benzenehexathiol (BHT) yields a large proportion of platinum nanoparticles PtNPs. Even addition of $\text{K}_3[\text{Fe}(\text{CN})_6]$ (same as for PdDT nanosheet) does not prevent the metallic Pt(0) formation. Thus, invention of a new synthetic technique is required. The reduction potential of benzenehexathiol is more negative



Scheme 2. Synthetic strategy for preparation of PtDT.

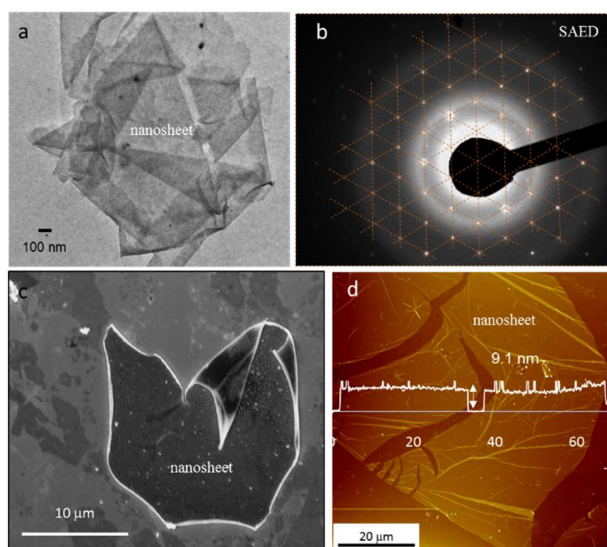


Figure 2. a. TEM image showing thin nanosheets without PtNPs and di-n-butyltin(IV) oxide, b. SAED of a showing hexagonal pattern, c. SEM image showing PtDT, d. AFM topography image for PtDT

than that of its thiolate counterpart; as a result, we need to employ the thiolate in the system, but the sodium salt of hexathiolate is easily oxidized in air. To avoid this problem, I introduced a transmetallation approach using a protected BHT, which was prepared as noted in Scheme 2. A liquid–liquid interfacial reaction of K_2PtCl_4 in an aqueous phase and tin-protected benzenehexathiolate (Sn-BHT) in an organic phase (dichloromethane) yielded a thin lustrous black film with 0.2-0.6 mm thickness (referred as SnPtDT). The product contained insoluble di-n-butyltin(IV) oxide, which was identified by XPS, AFM, IR, SEM-EDS and TEM imaging, but PtNPs were not detected. The insoluble agglomerate of di-n-butyltin(IV) oxide was separated by the ligand exchange reaction.

Removal of the tin compound was evidenced by XPS, IR, AFM, SEM-EDS and TEM (the pure Pt dithiolene nanosheets is referred as PtDT).

XPS analysis of PtDT revealed the existence of each element (S, Pt, C) and that the oxidation state of PtDT is 0. The layered material was exfoliated in hydrophobic Si(100) and was seen under AFM. Large smooth area of more than $50\ \mu\text{m} \times 50\ \mu\text{m}$ with less than 10 nm thickness was observed. SAED results gave perfect hexagonal diffraction points proving that the PtDT have hexagonal packing.

Exploring hydrogen evolution reaction (HER) is also a prime objective of my research. The metalladithiolene MDT (M=Ni, Pd and Pt) nanosheets have been used as a site for HER reaction. The higher electro-catalytic properties of such metalladithiolene was observed in lower pH in the order of PtDT>PdDT>NiDT. The electrocatalytic potential for all the CONASH material was in positive potential showing the low energy path for the HER reaction, yet there are chances to improve the efficiency of such materials by doping. The conductivity experiments were carried out showing the PtDT to be an insulator but under electron beam irradiation or thermal annealing techniques it is possible to increase the conductivity, yet it is still inconclusive about the structural changes on application of external energy.

Lastly, on successful synthesis of the PtDT, it is important to extend from group 10 series to group 11 elements capable of forming square planar coordination complexes. I tried to synthesize the Au-BHT thin films using interfacial reactions. But the similar redox problem was faced which needs to be addressed with different synthetic strategies. An ambiguity in structure still persists which needs further research as it is more challenging than group 10 metal bis(dithiolene) nanosheets.

Conclusion

The expansion of group 10 metals with BHT ligand system was successful with Pd and Pt. The synthetic procedures were entirely changed from nickelladithiolene nanosheet because the reaction of the noble metal ions with considerably positive reduction potentials and benzenhexathioliol ligand with non-innocent nature forms metal nanoparticles (MNPs). Eventually, new methods of successful formation of PdDT and PtDT were established. Particularly in case of PtDT, liquid-liquid exfoliation was achieved and chemical removal of insoluble di-n-butyltin(IV) oxide from the insoluble coordination polymer was accomplished. The obtained coordination nanosheets were fully characterized with XPS, TEM, SAED, SEM, AFM, and IR. At last, the hydrogen evolution reactions using MDT (M=Ni, Pd and Pt) were also explored proving that this multinuclear planar framework can be a site for electrocatalysis.