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Diethyldithiocarbamate Chelates as Eco-Friendly Precursors to Sustainable Metal Chalcogenide for Energy Storage Applications

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Abstract- The production of energy from nonrenewable resources is currently a major concern due to issues including ozone layer depletion, water pollution, global warming, environmental degradation, and the rise of new diseases. The increasing demand for energy transfer technologies and energy storage devices has obtained significant attention worldwide. In the field of inorganic chemistry, binary, ternary, quaternary, and multinary metal sulfides have been praised for their potential in energy conversion and storage. Metal complexes function as a precursor for metal chalcogenides based on their structure, stability, and thermal breakdown. Since structure and energy are two of the fundamental characteristics of molecules, they represent important concepts in modern chemistry. The synthesis of metal chalcogenide nanoparticles using single source precursors (SSP) has several advantages over alternative techniques. This article discusses the usage of diethyldithiocarbamate chelates as a single molecular precursor for a variety of metal sulfides, both binary and multicomponent. The use of these generated sulfides for energy storage is also covered.

Keywords- *Metal Complexes, Single Source Precursor, Metal Sulfide, Energy Storage.*

I. INTRODUCTION

Ozone layer depletion, water pollution, global warming, environmental degradation, and the appearance of new diseases are some of the issues that have made energy production from nonrenewable resources a serious concern nowadays [1]. So, renewable energy sources can effectively replace the finite energy supplies derived from fossil fuels. The increasing demand for energy transfer technologies and energy storage devices has obtained significant global attention [2]. Utilizing electrochemical energy storage to address the scarcity of renewable energy sources is important in this era of increasing energy consumption [3,4].

Transition metal chalcogenides and oxides have outstanding electrochemical output for use in energy conversion and storage, photovoltaics, high-temperature superconductors, sensors, and catalysis [4,5]. For instance, they have remarkable mechanical, electrical, thermal, optical, and catalytic properties [3]. Metal sulfides are typically selected over metal oxides due to their unique stability, effectiveness, sustainable production, and practicality in terms of cost [3,4].

The ability of binary, ternary, quaternary, and multinary metal sulfides to convert and store energy has been praised in the field of inorganic chemistry [1,6,7]. These compounds are a class of inexpensive materials that have potential uses in a variety of fields, such as solar cell applications, energy storage, and imaging [6]. Also, they have high electrochemical activity, outstanding redox reversibility, capacitance, conductivity, and electrocatalysis [1]. Metal complexes function as a precursor for metal chalcogenides based on their structure, stability, and thermal breakdown [1,8]. Since structure and energy are two of the fundamental characteristics of molecules, they represent important concepts in modern chemistry [9].

The synthesis of metal chalcogenide nanoparticles using single source precursors (SSP) has several advantages over alternative techniques. These include low toxicity, minimal or no pre-reactions and contamination, and ligand selection that can affect volatility [8]. Also, employing SSP becomes an imperative synthetic approach for only a minority of sulfur-based ligands such as ethyl xanthate, thiobenzoic acid, thioethers, and diethyldithiocarbamate as it depends upon the ligand system [10]. The application of diethyldithiocarbamate complexes as single molecular precursors (SMPs) to a broad range of binary and multicomponent metal sulfides is represented in this review. Additionally, the usage of metal sulfide for energy storage is the main emphasis of this work.

II. DIETHYLDITHIOCARBAMATE COMPLEXES AS SSP

Diethyldithiocarbamate belongs to the class of monoanionic 1,1-dithiolate ligands [11]. The formation of Diethyldithiocarbamate salt is an exothermic reaction and therefore, normally conducted at an extremely low temperature (ice bath) [12]. In Figure 1, a nucleophilic attack occurs between secondary amine (diethylamine) with carbon disulfide in water or alcoholic solution in basic medium or excess amine [13].
Diethyldithiocarbamic acid (Et_2NCS_2H) is highly unstable and decomposes under acidic conditions to an amine and carbon disulfide [8,14]. So, the ligands are usually isolated as their alkali metal or ammonium salts by using a base acting as a proton acceptor. Also, the alkali metal salt of diethyldithiocarbamate is water soluble with limited solubility

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in organic solvents while their ammonium salts are more soluble in an organic solvent [15].

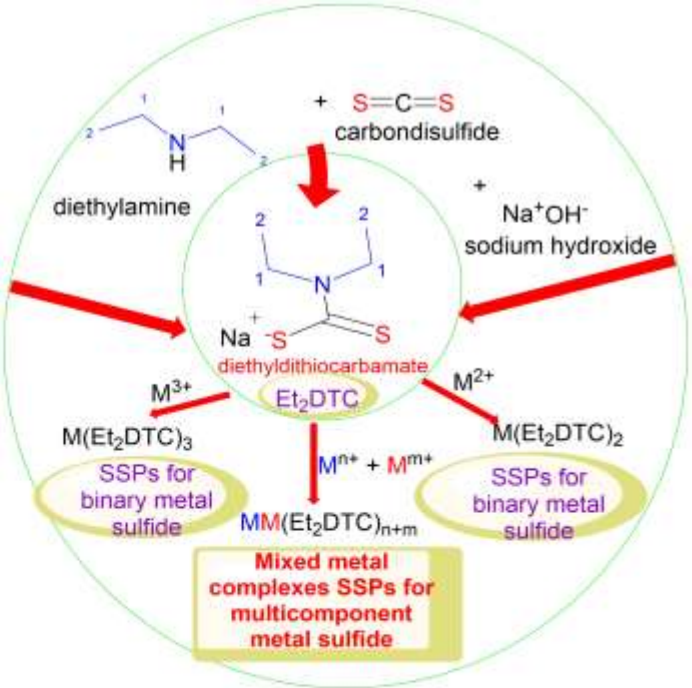

Figure (1): Schematic illustration of the synthesis of diethyldithiocarbamate anion and complex formation

The formed diethyldithiocarbamate anion, Figure 1, is a remarkably effective ligand for metals and poses different coordination modes to stabilize various oxidation states [8,14]. Because of diethyldithiocarbamate ligands are expressed by four resonance structures as shown in Figure 2 [16]. The stability of an SSP is determined by the ligand system [10]. For example, diethyldithiocarbamate complexes are considered good SSPs due to their stability, stronger metal-sulfur and carbon-sulfur bonds, volatility for chemical vapor deposition (CVD) [6], and a larger electron-donating $-NR_2$ group (thioureide group) [10].

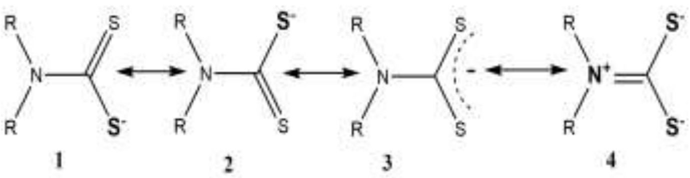

Figure (2): Resonance structures of dithiocarbamate anion

III. BINARY METAL SULFIDES AND THEIR APPLICATION

Metal sulfides in particular, a variety of sulfur-containing ligands are readily adjustable, and altering their characteristics allows for regulated alteration of the secondary breakdown products and decomposition rates. Thiolates, thioureas, xanthates, and dithiocarbamates (DTCs) are a few examples that have been extensively studied. Another benefit is that some of these ligands also function as surfactants, self-capping to stabilize the produced nanocrystals. There are two distinct SSP breakdown regimes: first solvothermal using a capping agent, and second chemical vapor deposition (CVD) (unless self-capping) [6]. In this review, our attention is focusing on the metal sulfide derived from the diethyldithiocarbamate ligand (Et_2DTC). For instance, green precursor zinc bis(diethyldithiocarbamate) served as a foundation for efficiently generating high-quality wurtzite ZnS nanoparticles through a solventless melt method, as confirmed by X-ray diffraction analysis, EDX, and SEM. The latter technique confirmed the poly-dispersed spherical and cubic structures of ZnS. While EDX reveals approximately a 1:1 Zn to S ratio [17].

Figure 3 illustrates the production of cobalt sulfide (Co_9S_8) nanoparticles (NPs) by solvothermal techniques employing a single-source precursor cobalt bis(diethyldithiocarbamate) (Co $[Et_2DTC]_2$) and hexadecylamine (HDA) as a capping agent. The improved Co_9S_8 NPs electrode produced remarkable specific capacitance equals to 502 Fg^{-1} at current densities of 1 Ag^{-1} and the capacitance retention reached 87% after 7,000 cycles [18]. In another work, copper bis(diethyldithiocarbamate) (Cu $[Et_2DTC]_2$) was used as the SSP in the solvothermal process to create CuS nanocubes (NCs) at low temperatures. HDA was used as a shape-directing agent. The electrochemical characteristics of a modified copper sulfide NCs working electrode were assessed using an electrolyte solution of 1 M potassium hydroxide. The modified CuS nanocubes electrode demonstrated an outstanding specific capacitance equals to 1472.3 Fg^{-1} at 1 Ag^{-1}, along with excellent capacitive retention up to 93.6% after 5,000 cycles at a current density of 10 Ag^{-1} [19].

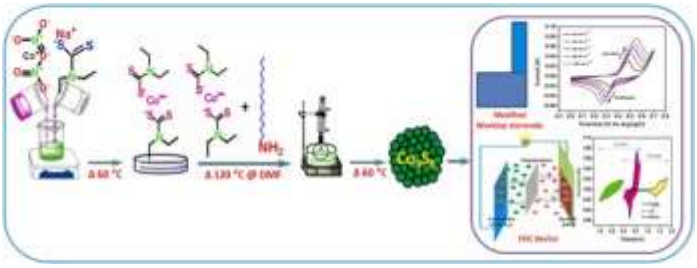

Figure 3 Schematic illustration of the synthesis of Co_9S_8 energy storage application, Adapted with permission from Ref. [18] (Copyright 2022, Elsevier)

IV. ENERGY STORAGE APPLICATION OF MULTI-COMPONENT METAL SULFIDES

A ternary composite of metal sulfide, or semiconducting tri-chalcogenide, was created using the single source precursor technique [3]. Figure 4 illustrates the detailed process used to prepare the tri-chalcogenide system from the diethyldithiocarbamate ligand. After The Et_2DTC ligand bound the metal salts, the metal complex solution was deposed on an electrode. Metal sulfide thin films were produced by the physical vapor deposition method with a resistive heating apparatus. Glass slides and fluorine-doped tin oxide (FTO) sheets were carefully cleaned to ensure optimal conditions for the deposition procedure [20]. Table 1 lists the recent tri-chalcogenide system synthesized by diethyldithiocarbamate SSP and used for energy storage applications [2,3,21-27]. It has been demonstrated that these sulfides make good electrode materials for energy storage with BaS_3: Ni_2S_3: Sb_2S_3 having the highest specific capacitance of 1019.4 F g^{-1}, Table 1.

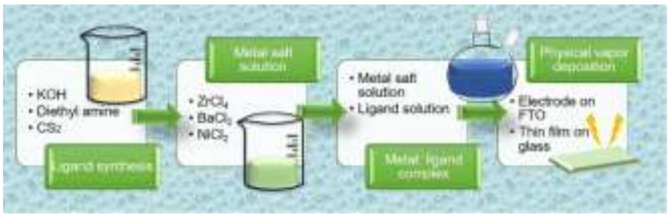

Figure (1): Preparation Scheme of tri-chalcogenide system, Adapted with permission from Ref. [20] (Copyright 2022, Elsevier)

Table (1): Recent tri-chalcogenide system for energy storage

Multicomponent system	specific capacitance (F g^{-1})	specific power density (W kg^{-1})	[Ref]
BaS: MnS: DyS	824.13	10826.7	[2]
BaS_3: Ni_2S_3: Sb_2S_3	1019.4	11931.26	[3]
BaS_3: Cu_2S: Mn_2S	694	10618	[21]
BaS: MnS: Sb_2S_5	762.83	9084.78	[22]
BaS_3: La_2S_3: $DyS_{1.8}$	723	11166	[23]
BaS: Sn_2S_3: LaS	659.6	3661.65	[24]
BaS_3: La_2S_3: Ho_2S_3	779	10145.28	[25]
BaS: CoS: La_2S_3	967.24	1659	[26]
BaS: NiS: Gd_2S_3	745.55	5674.08	[27]

V. CONCLUSION

Diethyldithiocarbamate is one of the most promising ligands for preparing metal sulfide by single precursor techniques. Also, the prepared metal sulfide had outstanding properties for various applications, such as photocatalysis, quantum dots, solar cells, energy storage, and water purification.

VI . ACKNOWLEDGMENT

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VII. REFERENCES

[1] M. P. Motaung and D. C. Onwudiwe, *Metal dithiocarbamates as useful precursors to metal sulfides for application in quantum dot-sensitized solar cell. In Sustainable materials and green processing for energy conversion.* Elsevier, 2022, 305-339.

[2] K. S. Ahmad, S. B. Jaffri, W. Lin, R. K. Gupta, G. A. Ashraf, and A. *El-marghany, utilizing sustainable trichalcogenide semiconductor BaS: MnS: DyS to maximize supercapacitor efficiency via innovative single-source precursor method*. Materials Chemistry and Physics, 2024, 325, 129720.

[3] S. B. Jaffri, K. S. Ahmad, B. Makawana, R. K. Gupta, M. A. Abdel-Maksoud, A. Malik, and W. H. Al-Qahtani, *amplifying energy storage and production efficiency: utilizing BaS_3: Ni_2S_3: Sb_2S_3 synthesized from dithiocarbamate precursors for enhanced and sustainable energy solutions.* Journal of Physics and Chemistry of Solids, 2024,112394.

[4] S. B. Jaffri, K. S. Ahmad, W. Lin, R. K. Gupta, G. A. Ashraf, and E. A. Al-Ammar, *sustainable in-situ synthesis of BaS_2: Cu_8S_5: LaS tri-metal chalcogenide via diethyldithiocarbamate precursors for high-performing energy storage systems.* Materials Science and Engineering: B, 2024, 307, 117537.

[5] P. Chandra, and M. Shaikh, *fabrication and catalytic applications of first row-transition metal and mixed-metal chalcogenides synthesized from single-source precursors.* In Nanomaterials via Single-Source Precursors, Elsevier, 2022, 389-451.

[6] J. C. Sarker, and G. Hogarth, *Dithiocarbamate complexes as single source precursors to nanoscale binary, ternary and quaternary metal sulfides*. Chemical Reviews, 2021, 121(10), 6057-6123.

[7] B. Akram, M. Aamir, A. S. Syed, and J. Akhtar, *flexible single-source precursors for solar light-harvesting applications.* In Sustainable Materials and Green Processing for Energy Conversion, Elsevier, 2022, 279-304.

[8] F. P. Andrew, and P. A. Ajibade, *metal complexes of alkyl-aryl dithiocarbamates: Structural studies, anticancer potentials and applications as precursors for semiconductor nanocrystals.* Journal of Molecular Structure, 2018, 1155, 843-855.

[9] R. Emara, M. S. Masoud, and S. Abboudy, *optical, electrical, thermal and kinetic studies for some pyrimidine ligands and their complexes.* Journal of Non-Crystalline Solids, 2022, 597, 121873.

[10] G. Karmakar, A. Tyagi, and A. Y. Shah, *a comprehensive review on single source molecular precursors for nanometric group IV metal chalcogenides: Technologically important class of compound semiconductors.* Coordination Chemistry Reviews, 2024, 504, 215665.

[11] E. J. Mensforth, M. R. Hill, and S. R. Batten, *Coordination polymers of sulphur-donor ligands*, Inorganica Chimica Acta, 2013, 403, 9–24.

[12] S. M. Lee and E. R. T. Tiekink, *A Structural Survey of Poly-Functional Dithiocarbamate Ligands and the Aggregation Patterns They Sustain*, Inorganics, 2021, 9(1), 7.

[13] A. Z. Halimehjani, K. Marjani, and A. Ashouri, *Synthesis of dithiocarbamate by Markovnikov addition reaction in aqueous medium*, Green Chemistry, 2010,12 (7),1306–1310.

[14] E. R. T. Tiekink, *Tin dithiocarbamates: applications and structures,* Applied Organometallic Chemistry, 2008, 22 (9), 533–550.

[15] G. Hogarth, *Metal-dithiocarbamate complexes: chemistry and biological activity*, Mini reviews in medicinal chemistry, 2012,12(12), 1202–1215.

[16] J. W. de F. Oliveira, H. A. O. Rocha, W. M. T. Q. de Medeiros, and M. S. Silva, *Application of*

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J. W. de F. Oliveira, H. A. O. Rocha, W. M. T. Q. de Medeiros, and M. S. Silva, *Application of dithiocarbamates as potential new antitrypanosomatids-drugs: approach chemistry, functional and biological*, Molecules, 2019, 24 (15), 2806.

S. A. Saah, P. O. Sakyi, N. O. Boadi, F. A. Tieku, and A. K. Boampong, *Solventless Synthesis of Zinc Sulphide Nanoparticles from Zinc Bis (diethyldithiocarbamate) as a Single Source Precursor*. ChemistryOpen, 2024, e202400050.

C. Sambathkumar, N. Nallamuthu, M. K. Kumar, S. Sudhahar, and P. Devendran, *Electrochemical exploration of cobalt sulfide nanoparticles synthesis using cobalt diethyldithiocarbamate as single source precursor for hybrid supercapacitor device*. Journal of Alloys and Compounds, 2022, 920, 165839.

C. Sambathkumar, K. R. Nagavenkatesh, K. M. Krishna, N. Nallamuthu, S. Sudhahar, and P. Devendran, *Electrochemical exploration on hexadecylamine capped copper sulfide nanocubes using single source precursor for enhanced supercapacitor devices.* Journal of Energy Storage, 2022, 56, 105898.

M. M. Gul, K. S. Ahmad, A. G. Thomas, and A. M. Tighezza, *From energy to environmental solutions: Harnessing ZrS: BaS: Ni_9S_8 thin film for supercapacitor and water purification.* Materials Science and Engineering: B, 2024, 303, 117340.

K. S. Ahmad, S. B. Jaffri, B. Makawana, R. K. Gupta, G. A. Ashraf, and N. H. Alotaibi, *Supercapacitor performance enhancement with the BaS_3: Cu_2S: Mn_2S trichalcogenide semiconductor synthesized via dithiocarbamate precursors.* Asia-Pacific Journal of Chemical Engineering, 2024, e3096.

K. S. Ahmad, S. B. Jaffri, J. S. Al-Hawadi, H. Panchal, R. K. Gupta, G. A. Ashraf, M. A. Abdel-Maksoud, and W. H. Al-Qahtani, *BaS: MnS: Sb_2S_5 Mixed Metal Chalcogenide Cubes: Synthesis, Characterization, and Exploring Energy Storage and Production Potential*. Applied Organometallic Chemistry, 2024, e7801.

S. B. Jaffri, K. S. Ahmad, J. S. Al-Hawadi, N. Maley, R. K. Gupta, G. A. Ashraf, and A. A. A. Bahajjaj, *Semiconducting BaS_3: La_2S_3: $DyS_{1.8}$ multinary metal chalcogenide hetero system prepared via single source precursor route: expounding energy storage potential.* Applied Physics A, 2024, 130(11), 800.

S. B. Jaffri, K. S. Ahmad, J. S. Al-Hawadi, W. Lin, R. K. Gupta, G. A. Ashraf, and N. H. Alotaibi, *Sleuthing the performance of the sustainable mixed metal trichalogenide BaS: Sn_2S_3: LaS from single source route as an electrode material for charge storage*. Ceramics International, 2024, 50(21), 42835-42845.

S. B. Jaffri, K. S. Ahmad, J. S. Al-Hawadi, B. Makawana, R. K. Gupta, G. A. Ashraf, and M. K. Okla, *Revolutionizing energy storage and electro-catalysis: unleashing electrode power with novel BaS_3: La_2S_3: Ho_2S_3 synthesized from single-source precursors for enhanced electrochemical functionality*. Journal of Sol-Gel Science and Technology, 2024, 1-16.

S. B. Jaffri, K. S. Ahmad, N. Maley, R. K. Gupta, G. A. Ashraf, and E. A. Al-Ammar, *High-Performance Electrode for Energy Storage Developed Using Single-Source Precursor-Driven Bas: Cos: La_2S_3 Trichalcogenide Semiconductor*. Physica status solidi (a), 2024, 221(20), 2400217.

K. S. Ahmad, S. B. Jaffri, W. Lin, R. K. Gupta, G. A. Ashraf, and A. M. Tighezza, *Electrifying sustainability: synthesis of BaS: NiS: Gd_2S_3 semiconductor trichalcogenides via single-source precursors for optimal supercapacitor operation.* Ionics, 2024, 30(10), 6425-6439.