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Recent Approaches for the Direct Use of Elemental Sulfur in the Synthesis and Processing of Advanced Materials

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composites · elemental sulfur · lithium–sulfur batteries · materials science · polymers

Elemental sulfur is an abundant and inexpensive material obtained as a by-product of natural-gas and petroleum refining operations. Recently, the need for the development of new energy-storage systems brought into light the potential of sulfur as a high-capacity cathode material in secondary batteries. Sulfur-containing materials were also shown to have useful IR optical properties. These developments coupled with growing environmental concerns related to the global production of excess elemental sulfur have led to a keen interest in its utilization as a feedstock in materials applications. This Minireview focuses on the recent developments on physical and chemical methods for directly processing elemental sulfur to produce functional composites and polymers.

1. Introduction

Sulfur is found in nature in its elemental form and has been used for thousands of years. Early uses of elemental sulfur include those for medicinal and pesticidal purposes and also as a component of gunpowder.[1] Today, sulfur is mainly used in the production of sulfuric acid, an important commodity chemical. Until the late nineteenth century, sulfur deposits in the volcanic rocks of Sicily were the largest source of elemental sulfur. The Frasch process,[2] patented in 1891, allowed the extraction of sulfur from the then newly discovered underground deposits in North America. The growth in global sulfur production was further accelerated by the need to remove sulfur, the third most abundant element in fossil fuel after carbon and hydrogen,[3] during refining to reduce sulfur dioxide emission and minimize catalyst poisoning during downstream processes.[4] In 1971, this "involuntary" production of sulfur from refining operations exceeded that from mining. The process for removing sulfur from natural gas and crude oil is known as hydrodesulfurization, or hydrotreating, and involves hydrogenation of crude oil and gas to produce, along with hydrocarbons, H_2S which is subsequently oxidized to sulfur through the Claus process.[5] This process leads to nearly all of the current global sulfur supply.

In recent years, an endeavor from the oil and gas industry to exploit sulfur-rich resources that had previously been deemed unprofitable, coupled with tightening regulations on the content of sulfur in transport fuels have caused a further expansion of the global sulfur production.[6] It is estimated that some seven million tons of excess sulfur are generated annually,[1] and it is generally accepted as a fact that the production will continue to grow.

While the problem associated with refining sulfur-rich oils and gases is a challenge in itself, dealing with the large quantity of resulting sulfur arguably presents an even greater challenge. Although there are ongoing attempts from the industry to address the issue, such as using sulfur as an additive in asphalt for road pavement,[7] the current use of sulfur apart from the production of sulfuric acid[8] and several other niche applications is nearly nonexistent, leading many major refiners, who are also the major sulfur producers, to store excess sulfur indefinitely in massive deposits in remote areas (Figure 1). While sulfur is widely considered to be

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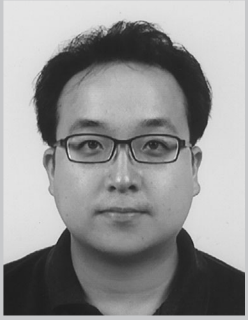
Figure 1. Above-ground deposit of excess elemental sulfur produced from the Claus process, reproduced from Ref. [82].

environmentally benign, the long-term effect of maintaining megaton quantities of elemental sulfur in fully exposed above-ground deposits has not yet been evaluated. It should also be taken into consideration that the exposed storage of sulfur is in itself potentially very dangerous, as it produces toxic sulfur dioxide upon combustion. Now, as we celebrate the 150th anniversary of BASF and the rich history of the chemical industry it represents, it seems to be an opportune moment to seriously consider the possibility of converting the stockpiles of sulfur into value-added materials.

Sulfur is by no means a useless material. It features a very high alkaline metal storage capacity per weight and is a promising material for cathodes of rechargeable batteries, including lithium–sulfur (Li–S)[9] and sodium–sulfur (Na–S) systems.[10] Sulfur-containing functional groups lead to a high molar refraction and are thus utilized for the synthesis of materials with high refractive indexes.[11] Sulfur-rich materials also exhibit high transparency in the IR region, which enables their application in IR optical materials.[12] Sulfur is also known to have pesticidal properties and is used as nontoxic pest control in the agricultural industry.[13] Crystals of α-sulfur, the most commonly found form of sulfur in nature, is also known to have photocatalytic activity.[14] Furthermore, the relatively weak S–S bond has been utilized in dynamic covalent chemistry.[15]

Despite the enticing characteristics of elemental sulfur and its numerous allotropes,[16] there are only a limited number of synthetic methods for the direct utilization of sulfur, and they typically result in ill-defined products. One method of circumventing such difficulties is the employment of activated sulfur-containing reagents for the synthesis of sulfur-containing materials, a topic discussed in a comprehensive review by Steudel.[17] Although reactive sulfur-containing reagents have been employed extensively in organic and materials chemistry, their usage is outside the scope of the direct utilization of elemental sulfur. Herein, the methods of the direct utilization of elemental sulfur are classified into two general categories. The first category consists of physical procedures that do not involve the chemical treatment of elemental sulfur, and the second consists of synthetic procedures involving the chemical treatment of elemental sulfur.

This Minireview is not intended to be a comprehensive overview of sulfur chemistry. Rather, it aims to provide chemists new to the field of sulfur and related chemistry with methods of utilizing elemental sulfur directly in the formation of novel polymers and functional materials. To this end, we limit our discussion to the methods in which elemental sulfur is used as the major component and plays an important role in the functions of the final product. Furthermore, while the Minireview focuses on reports from the past twenty years, some important work predating this time period is also provided where necessary.



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2. Physical Processing of Elemental Sulfur

Li–S batteries have thus far been the main area of modern applications of sulfur-derived composite materials. With the recent progress in the controlled syntheses of functional nanostructures, significant improvements on the conductivity and recyclability of sulfur-based cathodes have been made in the form of nanocomposites.[18] While the reader is referred to a detailed review for a full discussion on Li–S batteries,[9] the following sections of this Minireview will focus on the methods utilized for the direct processing of elemental sulfur in the formation of composite materials. These methods are further divided by the phase in which the sulfur exists during processing (liquid, vapor, or solution). The speciation of sulfur varies with the phase and temperature, a characteristic that could be exploited to control, for example, the equilibrium potential of sulfur composites in Li–S batteries. Also, the chemical behavior of sulfur is known to change in a confined environment,[19] which are aspects that merit consideration when designing sulfur-derived materials.

2.1. The Melt-Diffusion Method

At the molecular level, α-sulfur consists of eight-membered rings of sulfur atoms in a crown-like conformation called cyclooctasulfur (Figure 2). Cyclooctasulfur melts at 119.6 °C,[20] and molten sulfur undergoes a sharp increase in viscosity at 159.4 °C,[21] referred to as the λ (or floor) temperature, as a result of the formation of linear polymeric sulfur.[22] The thermal behavior of sulfur was recently investigated extensively.[22,23]

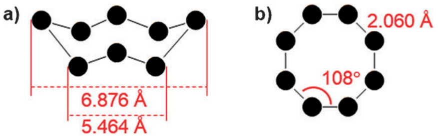


Figure 2. Structure of cyclooctasulfur with a) representing the conformation and dimensions as adapted from the calculations in Ref. [38], and b) showing the bond length and S–S–S bond angle, adapted from Ref. [20]. Black spheres represent sulfur atoms.

One of the most widely used physical methods to prepare sulfur composites is the melt-diffusion process in which a mixture of solid sulfur and a host material is heated to about 150 to 155 °C to induce the diffusion of sulfur into the host matrix.

In 2009, Nazar et al. first reported the melt-diffusion procedure to form mesoporous (2–50 nm pores)[9] carbon/sulfur nanocomposites.[24] A mesoporous carbon, CMK-3,[25] was mixed with an appropriate amount of sulfur and subsequently heated to 155 °C to induce the diffusion of sulfur into the carbon matrix (Figure 3). The composite showed a markedly enhanced capacity compared to a simple mixture of CMK-3 and sulfur in coin-cell tests. A similar melt-diffusion method was subsequently reported for the preparation of sulfur composites with ordered mesoporous carbon (OMC),[26] bimodal mesoporous carbon,[27] spherically ordered mesoporous carbon,[28] carbon fiber cloth,[29] mesoporous carbon/silica mixture,[30] mesoporous carbon/multi-walled carbon nanotube composite,[31] macroporous carbon,[32] hollow porous carbon,[33] nitrogen-doped porous carbon/CNT hybrid,[34] hierarchically porous carbon,[35] and vertical hollow carbon arrays.[36]

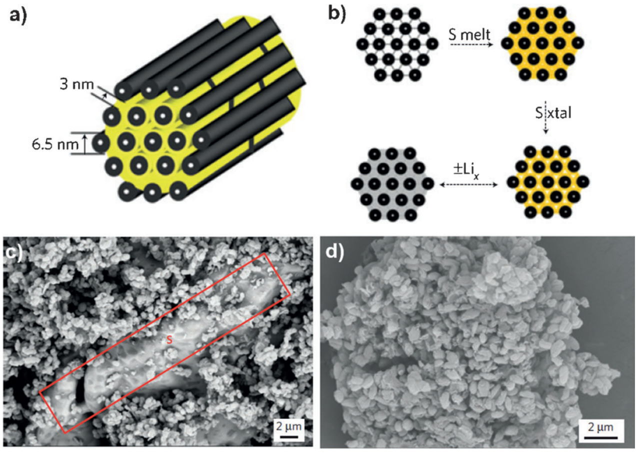


Figure 3. a) Schematic illustration of melt-diffusion process for sulfur nanocomposite synthesis, b) sulfur/CMK-3 composite obtained using this method, and SEM images of a sulfur/CMK-3 mixture c) before and d) after the melt-diffusion process. Reprinted with permission from the Nature publishing group Ref. [24].

Sulfur–carbon composites with microporous carbon, in which the pore size is below 2 nm,[9] were also achieved using the same melt-diffusion method. This result is interesting because the dimensions of cyclooctasulfur (Figure 2) may be larger than some of the pores. In 2010, Gao et al. reported composites of sulfur and microporous carbon with a sulfur content of up to 42 wt %, which were prepared by the melt-diffusion method.[37] The authors claimed that the small pore size effectively prevented the loss of sulfur from the composites during the battery operation. The method was also used to infuse elemental sulfur into carbon nanotube (CNT)/microporous carbon frameworks, the average pore size of which was about 0.7 nm, and it was later suggested that in the composite the sulfur exists in short, linear chains to fit into the pores, leading to the disappearance of the plateau at 2.3 V (versus Li), which, from the galvanostatic discharge curve of the material, is attributed to the reduction of S_8.[38]

Recently, the melt-diffusion method was adopted to obtain sulfur composites with metal–organic frameworks (MOFs), such as MIL-100(Cr)[39]/S[40] and HKUST-1(copper/benzene-1,3,5-tricarboxylic acid)/S composites.[41]

2.2. Vapor-, Solution-, and Dispersion-Based Methods

Elemental sulfur has a relatively low enthalpy of vaporization (≈ 2.5 kcal mol^{-1}) and sublimation (≈ 2.9 kcal mol^{-1}), allowing the element to be readily processed in the vapor phase.[20] The vapor-phase processability of sulfur has been exploited to address the issue of a possible loss of liquid elemental sulfur from the composite materials either during processing or during the operation of Li–S batteries. Furthermore, the speciation of sulfur in the vapor phase[42] varies with temperature, with sulfur gas mainly containing S_8 and S_6 at 200 °C and S_6 and S_2 at 600 °C.[43] This allows some control over sulfur speciation in the final products.

The vapor-phase analogue of the melt-diffusion process, known as the vapor-phase infusion method,[44] involves the heating of host-matrix/elemental-sulfur mixtures at various temperatures (approximately 160 to 500 °C) in vacuum-sealed tubes. A discharge curve obtained from disordered CNT/sulfur composites formed by this method at 160 °C[44] showed the potentials corresponding to the reduction of S_8 to S_6^{2-}, S_4^{2-}, and S_2^{2-}. The discharge curves of the composites prepared at 300 °C showed significantly reduced plateaus at 2.45 and 2.15 V (versus Li), which were nearly eliminated for the composites prepared at 500 °C. These changes were attributed to the state of sulfur changing from S_8 to S_6 to S_2 in the composites with the increase in processing temperature.

Vapor-phase infusion was also utilized to form porous hollow carbon/sulfur composites.[45] Subjection of open-ended single-walled and double-walled CNTs to the vapor-phase infusion gave sulfur chains inside carbon nanotubes (Figure 4).[46] This linear sulfur was claimed to assume a metallic phase,[16,47] which was previously only observed for elemental sulfur in the ultrahigh pressure range.

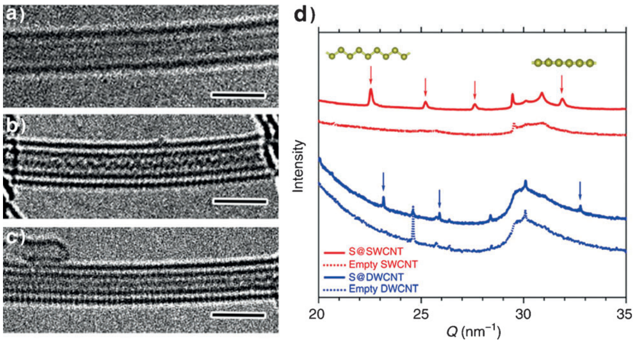


Figure 4. High-resolution transmission electron microscopy images of linear sulfur inside a) a single-walled CNT, b) a double-walled CNT in a zigzag conformation, and c) a DWCNT. d) XRD profiles of sulfur in SWCNT and DWCNT. Reprinted with permission from the Nature publishing group Ref. [46].

The third method of physical processing of elemental sulfur to form nanocomposites exploits the high solubility of elemental sulfur in CS_2. Liang et al. also reported the preparation of mesoporous carbon/sulfur composites by the repetitive solution impregnation and drying procedure involving a solution of sulfur in CS_2.[48] A similar method was used to prepare MOF-graphene oxide/sulfur composites.[49]

Colloidal particles of elemental sulfur or its derivatives have also been utilized to form nanocomposites. Elemental-sulfur powder, dispersed in an organic solvent, was utilized as the core onto which in situ synthesized polythiophene (PTh) was coated (Figure 5).[50] The method also allowed the control over sulfur content in the composites, and composites with higher than 80 wt % sulfur have been obtained.

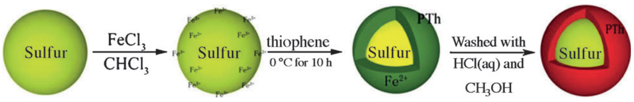


Figure 5. Illustration of the method utilized to coat the surface of elemental sulfur powder with a conjugated polymer, polythiophene. Reprinted with permission from the American Chemical Society Ref. [50].

The physical processing of elemental sulfur provides facile methods of the formation of functional composites. Furthermore, control over the electrochemical properties was demonstrated by decreasing the pore size of a host used in the melt-diffusion process or by simply changing the processing temperature during the formation of the nanocomposite in the vapor-phase infusion process. Various difficulties and the high cost of preparing nanostructured hosts are the issues to be overcome, but the ease of physical processing of elemental sulfur beckons for applications beyond electrochemically active composites.

3. Chemical Modification of Elemental Sulfur

The physical processing methods discussed in the previous section have led to a myriad of sulfur composite materials. However, the methods were developed for specific applications, which makes their implementation in large-scale manufacturing difficult. The current section outlines the chemical methods utilized for the modification of sulfur into useful materials. These methods can be divided into two general categories, processes involving anions and those involving free radicals. The methods constitute synthetic procedures that involve the direct use of elemental sulfur with a high potential for future applications.

3.1. Procedures Involving Anions

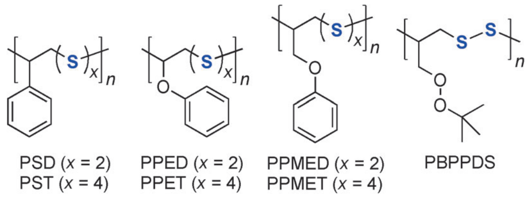
One form of sulfur found in nature[51] is that as linear dianions of the formula S_n^{2-}, generally called inorganic polysulfides. They can be formed in various ways, including the direct dissolution of elemental sulfur in an aqueous sodium sulfide solution.[52] The terminal sulfide anions are highly nucleophilic, which allows polysulfides to participate in nucleophilic sulfuration reactions and in polycondensations. The preparation, properties, and structure of inorganic polysulfides as well as polysulfide radical anions are discussed in a comprehensive review by Steudel.[53]

Polysulfides prepared by the dissolution of elemental sulfur in sodium sulfide solutions assume an average formula of Na_2S_x, where x is called the "rank" of the polysulfide and is determined by the molar ratio of Na_2S and added sulfur. Polysulfide solutions contain a complex mixture of anions of the formula HS_nS^- and S_n^{2-}, the distribution of which depends strongly on factors such as temperature, concentration, and pH value of the solution.[54] The cause of the diversity is attributed to the equilibria between polysulfides of varying lengths.[53] The direct speciation of polysulfide solutions had previously been difficult because of the disintegration and/or redistribution of the anions during analysis and it was assumed that the solutions consisted of di-, tri-, tetra-, and pentasulfides. More recently, a novel approach involving the fast methylation of polysulfide anions in aqueous solutions by methyl trifluoromethanesulfonate and subsequent analysis of the products by HPLC showed that hepta- and even octasulfide anions are present, suggesting the presence of even higher sulfides below the detection limits.[55]

The earliest example of a material prepared from elemental sulfur via inorganic polysulfides is a polycondensation product commercialized under the trade name Thiokol, which was obtained using organic halides and aqueous polysulfides.[56] Because of the immiscibility between aqueous polysulfide solutions and organic halides, the reaction proceeded through interfacial polycondensation, with cationic surfactants accelerating the product formation. Thiokol polymers were of note because of their high chemical resistance.[57]

The high chemical resistance of the polymers also meant a lack of suitable solvents for solution processing, thus limiting the further application of the chemistry outside industrial applications of compression-molded articles.[58] Readily processable polysulfide polymers were desired, as the labile S–S bonds in these materials could be utilized for an array of applications, including polymeric chain-transfer agents[59] and high-energy-content solid polymer fuels.[60]

Recently, various soluble polycondensates of polysulfide anions and organic dihalides were reported (Scheme 1). Kishore et al. reported polycondensation products between polysulfide anions of rank 2 and 4 with 1-phenyl-1,2-dibromoethane (styrene dibromide).[61] These polymers, poly(styrene disulfide), PSD, and poly(styrene tetrasulfide), PST, had a much higher onset temperature (220 °C) of thermal degradation compared to that of their oxygen analogue, poly(styrene peroxide) (110 °C). Treatment of PSD and PST with triphenylphosphine (PPh_3) induced chemical degradation through the initial nucleophilic attack by the phosphine and the subsequent inter- and intramolecular disulfide exchange reactions. PST, featuring the weaker tetrasulfide linkage, was shown to degrade spontaneously at room temperature upon the addition of PPh_3, while PSD decomposed under the same conditions at a higher temperature.[62] Both PSD and PST were adopted as chain-transfer agents for the radical polymerization of styrene.[63] When PSD was used, the rate of styrene polymerization did not vary much with the PSD concentration, but with PST, the rate of polymerization significantly decreased with the increase in PST concentration. This observation was attributed to the fact that RS· radicals are more reactive than RSS· radicals, which are resonance stabilized. The chain-transfer behavior of PSD and PST allowed their application as stabilizers against the thermal degradation of PMMA.[64]

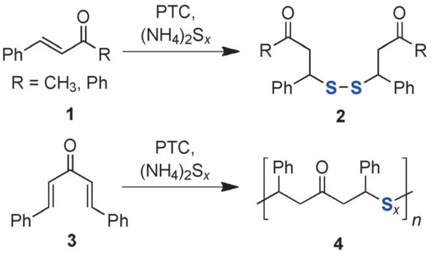


Scheme 1. Chemical structures of recently reported soluble polymers obtained through polycondensation between polysulfides and dihalides. PSD and PST are from Ref. [61]. Poly(1-(phenoxy)ethyl disulfide), poly(1-(phenoxy)ethyl tetrasulfide), poly(1-(phenoxymethyl)ethyl disulfide), poly(1-(phenoxymethyl)ethyl tetrasulfide) (PPED, PPET, PPMED, and PPMET, respectively) are from Ref. [65]. Poly(3-(5-butylperoxy)-propyl disulfide) (PBPPDS), is from Ref. [67].

Ramakrishnan et al. reported the synthesis of polycondensation products of rank 2 and 4 polysulfides with 1-phenoxy-1,2-dibromoethane (PPED and PPET, Scheme 1) and 1-phenoxy-2,3,-dibromopropane (PPMED and PPMET) and studied their main-chain flexibility in comparison to the corresponding polymers with a single sulfur atom per repeat unit by ^{13}C NMR spin-lattice relaxation-time measurements on the backbone carbon atoms of the polymers.[65] Interestingly, the results showed a reduced main-chain mobility with an increasing polysulfide rank, a trend that is opposite to that of the corresponding oxygen analogues, poly(styrene oxide) and poly(styrene peroxide). This observation was attributed to the delocalization, involving empty d-orbitals, of unpaired electrons on the sulfur atoms, a phenomenon that increases the barrier of rotation around the S–S bond.[66] A disulfide polymer with a pendant peroxide moiety was also synthesized (PBPPDS, Scheme 1).[67] The polymer was utilized as a macroiniferter in the synthesis of PS/PMMA copolymers. Compared to the polycondensation products of 1,2-dichloroethane with polysulfides, which contain over 70 wt % sulfur, the soluble polymers have a sulfur content of 55 wt % or less, suggesting that the sulfur content in the polysulfide polymers may play a role in determining the solubility.

In 1978, Penczek and co-workers reported the anionic copolymerization of elemental sulfur with propylene sulfide.[68] The polymerization proceeded through a ring-opening mechanism initiated by $CdCO_3$. Soluble polymers with presumably up to five sulfur atoms between the hydrocarbon units were obtained and characterized by ^1H and ^{13}C NMR spectroscopy. Although the molecular weights of these polymers were not discussed in detail and the exact number of sulfur atoms per repeat unit was controversial,[69] the potential for using elemental sulfur directly under anionic polymerization conditions in polymerizations other than polycondensations has been suggested nevertheless.

Polysulfide anions are also known to undergo conjugate-addition reactions with α,β-unsaturated ketones (Scheme 2).[70] With compounds that contain one α,β-unsaturated ketone moiety per molecule (**1**), dimers (**2**) were observed to be the major products. Interestingly, the diastereomeric ratio of the dimers varied with the reaction temperature and the solvent. When 1,5-diphenyl-1,4-pentadien-3-one (**3**) was used, however, polymer **4** was obtained as the major product. The polymers contained 24–28 wt % of sulfur,



Scheme 2. Reaction between α,β-unsaturated ketones and polysulfides under phase-transfer catalysis with didecyldimethylammonium bromide (DDAB).

suggesting the presence of di- and trisulfide linkages. Although the polymers were not characterized further, the chemistry provides an attractive alternative to dihalide polycondensation and allows the introduction of novel functional groups.

In summary, synthetic methods that involve polysulfide anions have led to various polymeric products. The increase in the length of the polysulfide units that comprise the polymer backbone strongly influences the physical and chemical properties of the polymer. Furthermore, the solubility of these polymers seems to depend on their sulfur content, with higher sulfur content leading to a reduced solubility. An analogy may be made with compounds containing fluoroalkyl groups, the high fluorine content of which leads to a reduced solubility.[71] While the molecular origins for such a behavior of fluorocarbons have been explored in detail,[72] analogous work on materials with a high sulfur content has, to the best of our knowledge, not yet been carried out. Furthermore, while there are fluorous solvents available for processing materials with a high fluorine content such as polymers,[73] no suitable solvent is known for the processing of sulfur-rich materials. It is desirable that, in the near future, these aspects of sulfur-rich polymers are further scrutinized along with the continued efforts on the synthesis of functional materials.

3.2. Processes Involving Free Radicals

The energy required to carry out the ring-opening of cyclooctasulfur, namely $S_8 \rightarrow {\cdot}S_8{\cdot}$, is about 36 kcal mol^{-1}.[74] The low barrier for the homolytic ring-opening of cyclooctasulfur renders the element capable of forming linear chains. Thus, the simplest polymeric material of sulfur is the linear form of sulfur itself, the formation of which causes the sharp rise in viscosity of molten sulfur above about 159 °C (Figure 6).

The polymer content in sulfur melts at different temperatures was determined directly by rapid quenching of molten sulfur at low temperature, followed by the extraction of low-weight fractions with CS_2 at 20 °C. The studies showed a sharp increase in polymer content above 159 °C.[75]

The polymers are thermodynamically unstable at room temperature and slowly revert to cyclooctasulfur. The linear-sulfur polymers have previously been studied in depth, but the direct use of linear sulfur for materials applications is scarce. In an exceptional report, Fréchet et al. demonstrated that the polymerization of elemental sulfur can be achieved by exposing a thin film of sulfur, spun-cast from a dilute chloroform solution, to a high electric field with a biased, conducting AFM probe.[76] After the formation of insoluble polymeric sulfur, untreated area composed of cyclooctasulfur can be simply washed off to obtain the desired patterns (Figure 7). It was also demonstrated that the patterned polymeric sulfur could be partially reduced to expose thiol moieties, which could be used as anchors for gold nanoparticles.

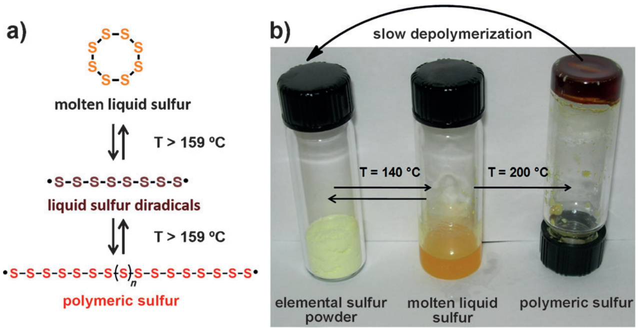


Figure 6. a) Simplified scheme of thermal ring opening and subsequent polymerization of cyclooctasulfur. b) Photograph of solid, liquid, and polymeric sulfur.

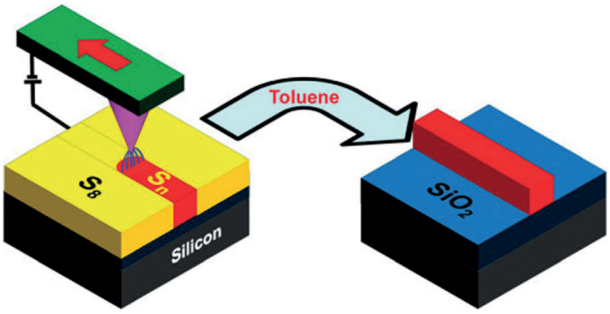
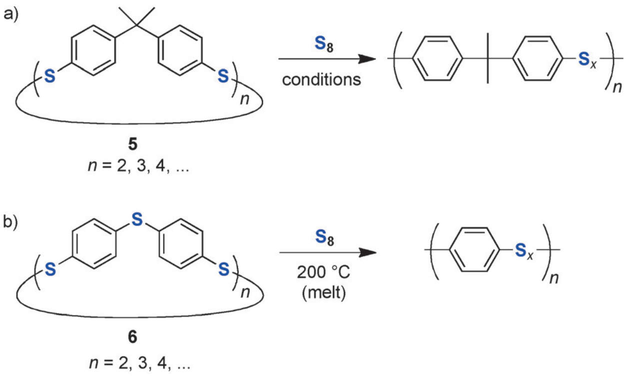


Figure 7. Polymerization of elemental sulfur using a conducting AFM probe and subsequent washing to form desired patterns. Reproduced from Ref. [76].

Many early attempts have been made to utilize molten sulfur as a reactant.[77] The resulting materials were characterized, when soluble, by NMR and other spectroscopic methods, but reliable estimates of their molecular weights were not available. In 1997, Hay et al. reported the radical copolymerization of elemental sulfur with oligomers of cyclic arylene disulfide (**5**, Scheme 3 a).[78] The solution copolymerization in diphenylether resulted in polymers with three to four sulfur units incorporated per repeat unit, regardless of the amount of sulfur added at the beginning of the reaction. When the reaction was conducted in molten sulfur, polymers containing sulfur units with higher ranks of up to seven were obtained. When three or four sulfur atoms were present per



Scheme 3. a) Polymerization of cyclic bis(benzenethiol) oligomer **5** with elemental sulfur. Heating at 150 °C in diphenylether resulted in $x = 3, 4$, and melt polymerization at 200 °C resulted in up to $x = 7$. b) Melt polymerization of cyclic 4,4′-thiobis(benzenethiol) oligomer **6** with elemental sulfur ($x = 1$–7).

repeat unit, the polymers were soluble in various organic solvents. However, the polymers with higher sulfur contents, obtained from molten sulfur, were insoluble in a wide range of organic solvents. The melt-polymerization method was also applied to cyclic monomer **6** for the preparation of poly(phenyl sulfide) derivatives with $x = 1$–7 (Scheme 3b). Analysis of these polymers showed that a higher sulfide rank led to lower T_g and tan δ values along with lower onset temperatures for thermal decomposition.

The concept of using a sulfur melt as a reaction medium and reactant was a new development in the preparation of materials with high sulfur contents. We previously demonstrated that molten sulfur could be used as a reaction medium for the synthesis of gold nanoparticles (Figure 8).[79] It was also discovered that the addition of divinylbenzene to the sulfur melt containing gold nanoparticles led to a fast vitrification of the medium and gave a dark, glassy, free-standing gold nanoparticle/sulfur polymer composite that did not revert to elemental sulfur upon standing. A similar polymeric matrix with sulfur and oleylamine was also obtained from molten sulfur.[80] Independently, Block et al. demonstrated the preparation of allylic-sulfide-terminated oligomers using liquid sulfur as the solvent and comonomer.[81]

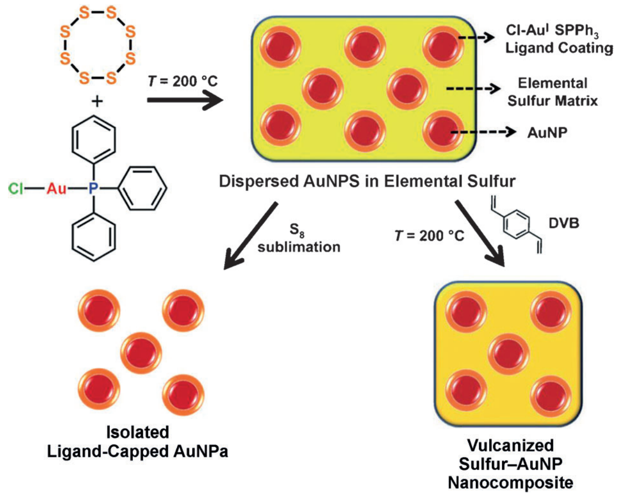


Figure 8. Synthesis of gold nanoparticles in molten elemental sulfur followed by either removal of sulfur by sublimation or treatment with divinylbenzene (DVB) to form cross-linked sulfur nanocomposites. Reproduced from Ref. [79].

While the nanocomposites of sulfur-based copolymers and nanoparticles are opaque and deeply colored materials, treatment of molten sulfur with diisopropenylbenzene (DIB) afforded glassy, red, transparent polymeric materials within minutes of the reaction at a temperature above 180 °C (Figure 9).[82] The materials were stable even at a very high sulfur content of over 90 wt % and did not revert to elemental sulfur upon standing. This synthetic method, dubbed "inverse vulcanization", could be scaled up to the kilogram scale.[83]

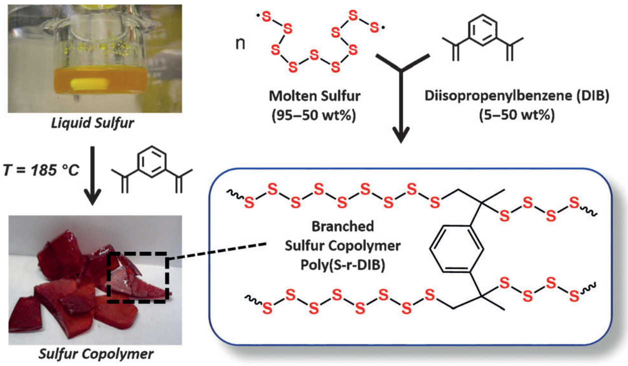


Figure 9. Copolymerization of diisopropenylbenzene with molten sulfur. Reproduced with permission from the Nature publishing group: Ref. [82].

The solubility in organic solvents could be controlled by varying the amount of added DIB, with polymers having higher DIB content exhibiting higher solubility in organic solvents such as *o*-dichlorobenzene. The glass-transition temperature and the performance as cathodes in Li/S batteries[84] could also be fine-tuned by controlling the ratio between sulfur and DIB. The polymer effectively prevented the formation of Li_2S dendrites at the cathode during the operation of Li–S batteries, an effect that was attributed to the plasticization of the Li_2S matrix by the DIB units.

These copolymers also have excellent IR transparency and high refractive indices, and could be readily processed into free-standing lenses (Figure 10)[12] by simply pouring the reaction mixture onto a heated mold and subsequently allowing to cool. The material could also be used for the thermal imaging of a person in the mid-IR region, and constitutes the first example of polymer lenses that are transparent at the corresponding wavelengths. More recently, a similar inverse vulcanization of 1,3-diethynylbenzene and elemental sulfur to similar cross-linked polymers was reported, thus demonstrating that the chemistry may also be utilized with monomers containing alkynyl moieties.[85]

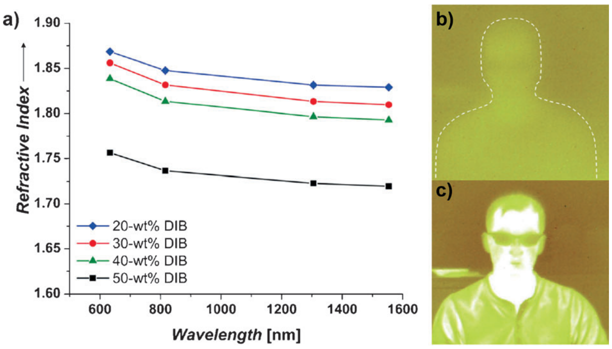


Figure 10. a) Average refractive indices of sulfur–DIB copolymers, and thermal imaging of a person in the mid-IR range (3–5 μm) through b) a PMMA film (≈1 mm) and through c) a film (≈1 mm) of sulfur–DIB copolymer with 20 wt % DIB. Adapted from Ref. [12].

Recent progress on the radical polymerization of elemental sulfur was made largely through the development of various ways of incorporating anchoring groups to prevent the depolymerization of sulfur-rich polymers to elemental sulfur.

Development of cross-linkable bisolefin monomers has led to a facile synthesis of polymers with very high sulfur content, giving both the electrochemical properties and high refractive index of sulfur. Although the requirement of relatively high temperature for the polymerization is a drawback, the utilization of sulfur both as a reaction medium and as a monomer may provide new areas of research and industrial applications.

3.3. Other Chemical Procedures

A few chemical methods for the processing of elemental sulfur were reported apart from the aforementioned anionic and radical procedures. Treatment of polysulfide solutions with graphene oxide (GO) in the presence of cationic surfactants induced the immobilization of sulfur onto GO through the formation of covalent bonds, and the composite material thus formed was applied as a cathode material in Li–S batteries.[86] The covalent bonds between sulfur and graphene were thought to have formed by the nucleophilic attack by polysulfide anions on the epoxide moieties and other electrophilic groups present on GO sheets.

The acidification of polysulfide solutions is also known to result in the precipitation of elemental sulfur. The reaction occurs through the formation of protonated polysulfides, or polysulfanes, which subsequently eliminate H_2S to form elemental sulfur following the reaction: $S_x^{2-} + 2H^+ \rightarrow (x-1)S + H_2S$. The method was adopted to prepare sulfur composites with carbon nanofibers[87] and graphene[88] in simple solution processes.

Another method of chemically modifying elemental sulfur involves the reduction of elemental sulfur with triethylborohydride to afford Li_2S or Li_2S_2.[89] Anhydrous metal sulfides were difficult to obtain, but the method provided an efficient route to anhydrous lithium sulfide for applications in a variety of reactions to form organic sulfides. Cairns et al. recently reported a utilization of this reduction to obtain Li_2S microspheres. The reduction gave Li_2S, which was subsequently coated with carbon to produce a robust composite for cathode materials for Li–S batteries in a fully discharged state (Figure 11).[90]

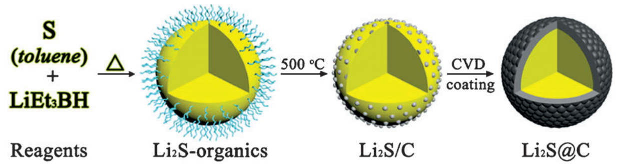


Figure 11. Schematic illustration of the synthesis of Li_2S nanoparticles by the reduction of elemental sulfur and subsequent surface coating. Reprinted with permission from the American Chemical Society Ref. [90].

While we attempted to provide an overview of important chemical modification strategies utilizing elemental sulfur, the literature discussed in this Minireview is by no means complete. For example, elemental sulfur is also directly utilized in the synthesis of metal chalcogenide nanoparticles, including quantum dots,[91] and in the synthesis of conjugated polymers such as polythiophenes from the transition-metal-catalyzed cycloaddition with diynes.[92] Although these methods utilize sulfur as a minor component or in large excess to compensate for inefficient reactions, they attest to the versatility of the direct utilization of elemental sulfur.

4. Outlook

The production of excess sulfur in refining operations is a critical issue to be addressed. In spite of many excellent studies on the physical chemistry of sulfur and polysulfides, which have led to a deeper understanding of this intriguing element, only a handful of reliable methods on the direct utilization of elemental sulfur in the production of advanced materials are available. The rich chemistry of sulfur, a glimpse of which was discussed herein, may lead to the development of novel strategies in this regard.

An important issue regarding sulfur-rich materials is the environmental concern with regard to their disposal. It is desirable to reuse the materials rather than stockpiling them in landfills (much like with elemental sulfur today), or, worse yet, incinerating them. Most recent developments in dynamic covalent chemistry, which exploit labile chemical bonds and/or reversible reactions, may provide interesting solutions, as evidenced by a number of examples in which S–S bonds have been utilized as a key component of this interesting concept.[93] The ability of S–S bonds to be thermally broken and rearranged may therefore enable the thermal recycling of sulfur-derived materials, much like in the recycling of thermoplastics.

The attractiveness of sulfur lies in the range of interesting properties the element provides. Most intriguing for a chemist may be the fact that the direct utilization of sulfur is still a largely uncharted territory.

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