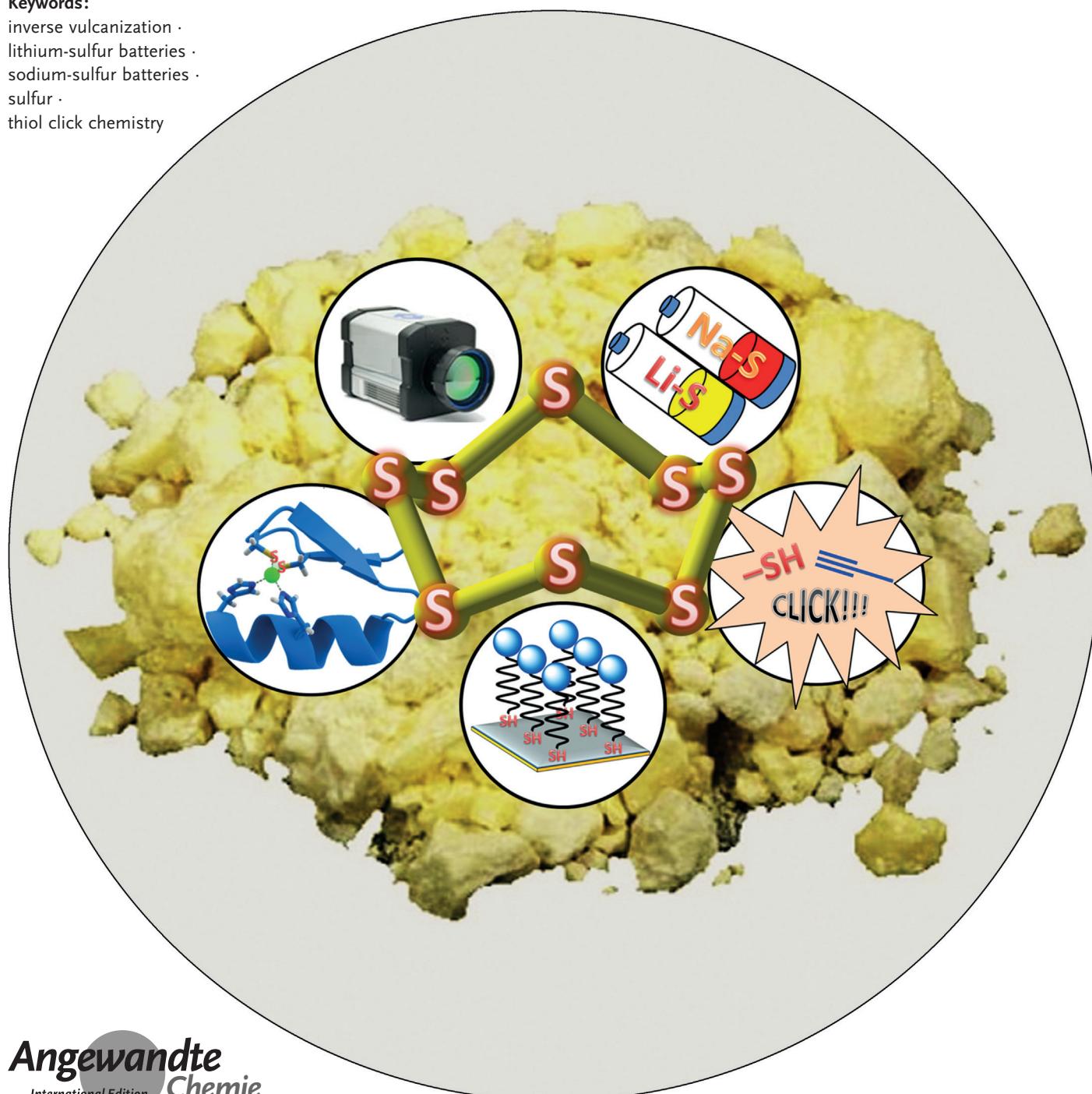


Sulfur and Its Role In Modern Materials Science

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Keywords:

inverse vulcanization ·
lithium-sulfur batteries ·
sodium-sulfur batteries ·
sulfur ·
thiol click chemistry



Although well-known and studied for centuries, sulfur continues to be at the center of an extensive array of scientific research topics. As one of the most abundant elements in the Universe, a major by-product of oil refinery processes, and as a common reaction site within biological systems, research involving sulfur is both broad in scope and incredibly important to our daily lives. Indeed, there has been renewed interest in sulfur-based reactions in just the past ten years. Sulfur research spans the spectrum of topics within the physical sciences including research on improving energy efficiency, environmentally friendly uses for oil refinery waste products, development of polymers with unique optical and mechanical properties, and materials produced for biological applications. This Review focuses on some of the latest exciting ways in which sulfur and sulfur-based reactions are being utilized to produce materials for application in energy, environmental, and other practical areas.

1. A Brief History of Sulfur

Elemental sulfur is incredibly Earth-abundant and has been mined for various uses for thousands of years. Until the early 1900s, the most common source of sulfur was the soil that surrounded volcanoes—principally the soil surrounding volcanoes on the island of Sicily in the Mediterranean Sea.^[1] As a consequence of its abundance, as well as its unique properties, sulfur has been a critically important asset for myriad products ranging from ancient bronze to 18th Century gunpowder to contemporary sulfuric acid.^[2]

During the early and middle parts of the 20th Century, many research efforts focused on understanding sulfur's phases.^[3] Sulfur exists as a yellow, orthorhombic crystalline solid at temperatures less than approximately 96°C.^[4] At temperatures between 96°C and 119°C, a monoclinic crystalline solid form of sulfur exists, although it maintains its yellow color.^[5] Both the orthorhombic and monoclinic versions of sulfur primarily contain sulfur in the form of S₈ rings, but the rings are packed differently to give the different crystal types.^[5] When heated to about 120°C, sulfur begins to melt into a yellow liquid. At around 159°C, a dramatic shift in its behavior occurs: chains of sulfur form as the S₈ rings begin to open and sulfur becomes an amorphous, viscous material.^[5,6] Further heating causes the viscosity to increase while its color darkens from yellow to orange and eventually to red.^[6] Instead of evaporating like many other elements do with increased temperature, the viscous sulfur polymerizes at about 200°C into a solid-like material that appears red in color.^[5] Upon cooling, these transitions occur in reverse, with the amorphous, red, solid-like polymer ultimately turning back into an orthorhombic yellow solid at low temperatures.^[6,7] It should be noted that even the color changes of sulfur have been a point of mystery and debate, with Meyer contending that polymeric sulfur is actually yellow, not red, in appearance when quenched as a thin film at 200°C.^[8] Meyer concludes that the overall red appearance arises from the presence of organic impurities, or the smaller sulfur molecules S₃ and S₄.^[8]

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Even with its unique temperature-dependent phases, elemental sulfur is generally benign. However, under the right conditions, sulfur is also well-known to form compounds with numerous other elements including lead to form galena (PbS), calcium to form gypsum (CaSO₄·2(H₂O)), iron to form pyrite (FeS₂), and even hydrogen to form harmful hydrogen sulfide gas (H₂S). Sulfur's ability to combine with so many other elements adds intrigue to the vast and varying ways in which it behaves, and to the element itself. This ability to combine with other elements also made sulfur difficult to extract and understand at an elemental level in times past.^[7] In fact, it was not until the 18th Century chemist Antoine Lavoisier began his work with sulfur that it was no longer considered a compound and was finally recognized as an element.^[9] Since that time, interest in sulfur, and the many ways in which it can be utilized, has flourished. From iron-sulfur clusters^[10] to molybdenum disulfide,^[11] from thiophene-based conducting polymers^[12] to the amino acids cysteine and methionine, sulfur is ever-present.

Today, elemental sulfur is primarily recovered as a major by-product of the oil refining and natural gas purification processes (Figure 1). It is estimated that more than 60 million tons of sulfur are produced every year.^[13] As a consequence of this, and as a result of sulfur's unique properties, there has long been a desire to take advantage of sulfur in energy-efficient and environmentally friendly ways.^[7] Thus, sulfur has become a major asset in modern polymer chemistry and materials science, while also becoming a focal point in research on alternative power sources. This Review will cover several of the major ways in which sulfur is currently being utilized in research, including vulcanization, rechargeable batteries, and thiol coupling reactions.

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 The ORCID identification number(s) for the author(s) of this article can be found under <http://dx.doi.org/10.1002/anie.201604615>.

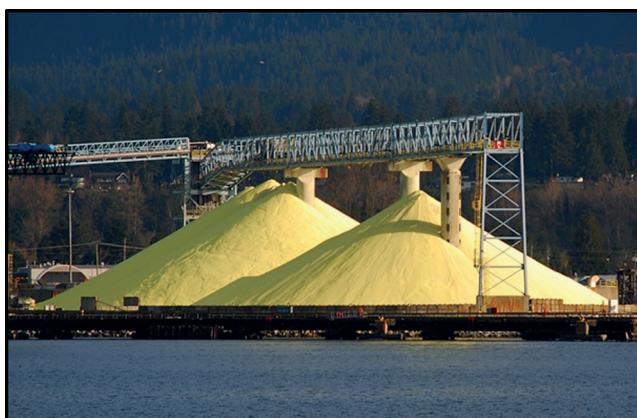


Figure 1. Massive stockpiles of sulfur at an oil refinery in Vancouver, Canada.

2. Modern Day Vulcanization

A principle use of sulfur is in the vulcanization of rubber. Vulcanization is the (generally) irreversible process by which rubber is converted into durable materials for use in a wide variety of applications through the cross-linking of sulfur and other additives. The discovery of the vulcanization process is often credited to Charles Goodyear in 1839.^[14] Natural rubber consists of polyisoprene chains that can freely move against one another, thereby leading to a sticky and easily deformable rubber material. Elemental sulfur can be introduced into the polyisoprene network of natural rubber as a cross-linker through vulcanization. These sulfur cross-links stabilize the overall structure and lend elasticity to rubber. Depending on the sulfur quantity and the quantities/types of other additives used to vulcanize rubber, vulcanized rubber can be soft or hard, stretchy or taut. Vulcanized rubber, in various forms, is used in numerous materials for practical everyday purposes including as tires, conveyor belts, soles of shoes, and saxophone mouthpieces. Although vulcanized rubber has been known for nearly two centuries, much of the more recent understanding of rubber and vulcanization stems from the extensive research of Arthur V. Tobolsky.^[5,6,15] His studies in this field were key to our present-day fundamental understanding of the aging, degradation, mechanical, and rheological properties of both sulfur and rubber, which ultimately

assisted in our understanding of the vulcanization process. Despite our current understanding, the widespread usage, as well as the significant value of rubber processing, vulcanization remains a difficult process and thus methods to improve it continue to this day.

2.1. Vulcanization

One way in which researchers are modifying the vulcanization process is by including renewable materials as cross-linkers. In one such example, Kato, et al. introduced cellulose nanofibers and sulfur into rubber.^[16] The cellulose nanofibers were functionalized with oleic acid, which is a long 18 carbon atom molecule with a single unit of unsaturation between the ninth and tenth carbon atoms in its structure. When sulfur was introduced, it served as a cross-linker between the polyisoprene units of the rubber and the oleic acids on the cellulose nanofibers. The product was a vulcanized rubber with enhanced mechanical properties, including a Young's modulus that was 15 times greater than that of natural rubber. This process is particularly interesting because cellulose nanofibers are renewable materials, their surfaces can be easily modified, and only 5 wt % of the oleyl-cellulose nanofibers was required to dramatically alter the mechanical properties. For these reasons, it is conceivable that cellulose nanofibers bearing other types of functional molecules (that can interact with sulfur) on their surfaces could be incorporated into vulcanized rubber and alter the properties of the rubber, even at low cellulose concentrations.

Using vulcanized polybutadiene as the proof-of-concept material, Zhang and co-workers recently reported that the sulfur cross-links within vulcanized rubber can be rearranged by the addition of copper(II) chloride (CuCl_2).^[17] The CuCl_2 served as a catalyst for the rearrangement of the sulfur, while the reaction itself produced no radicals or ionic intermediates. The benefits of this process include the ability to reprocess vulcanized rubber, perhaps leading to alternative rubber recycling methods and longer usage lifetimes of vulcanized rubber. If successful commercially, a process such as the one described by Zhang and co-workers could decrease the large amounts of rubber that are discarded as waste each year.

Imbernon et al. reported a method for the rearrangement of disulfide linkages within epoxidized natural rubber (ENR).^[18] They used a disulfide cross-linker that efficiently linked the backbone to form a high-molecular-weight ENR. The behavior of the product was similar to that of natural rubber at temperatures up to 100°C, but interestingly the material can be reprocessed at temperatures greater than 150°C. This was demonstrated by the grinding of the ENR into a powder and then reheating it to 180°C for 40 mins (Figure 2). Several analytical techniques were used to determine the mechanical properties of the reprocessed ENR, including dynamic mechanical analysis and gel-permeation chromatography. These analyses demonstrated that a significant portion of the mechanical strength can be recovered following the reprocessing of the material (Figure 2).

As one can see, the process of vulcanization continues to evolve, with the reprocessability of altered rubber products



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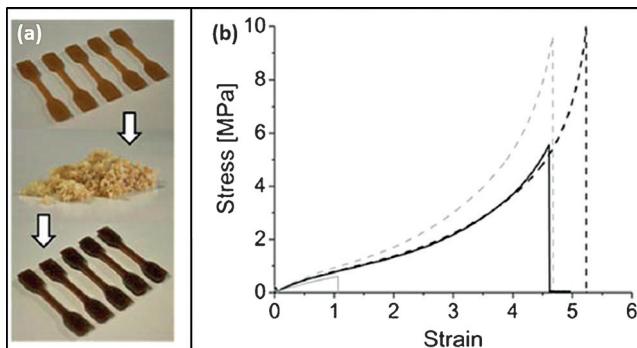


Figure 2. a) Cured and shaped ENR is finely ground, reshaped, and cured again. b) Tensile data showing that much of the mechanical strength is recovered following the reprocessing of the ENR (dashed line: before reprocessing, solid line: after reprocessing). Reproduced with permission from The Royal Society of Chemistry.^[18]

and improved mechanical properties being the central foci. If rubber cross-links can indeed be reversed and the rubber reprocessed, then this means rubber can be recycled. As the planet is extensively littered with rubber waste, the recycling of rubber has been a long-sought-after and environmentally friendly goal. Reports such as the ones described above are aiding in making that goal more plausible.

2.2. Inverse Vulcanization

In a creative reversal of the established vulcanization process, Pyun and co-workers reported in 2013 a process they termed “inverse vulcanization”.^[13,19] In this process, sulfur served as the backbone material, and aromatic carbon co-monomers were bound to sulfur chains to form stable polymer complexes. The inverse vulcanization method takes advantage of sulfur’s ring-opening and chain-forming tendencies at elevated temperatures by binding divinyl molecules to the sulfur radicals that form when sulfur’s S_8 rings open (Figure 3). Perhaps most noteworthy was the use of molten elemental sulfur itself as the solvent. The initial report utilized 1,3-diisopropenyl benzene (DIB) as the co-monomer because of its available divinyl groups and high boiling point (ca. 230 °C). The resulting polymers were given the name poly(sulfur-random-(1,3-diisopropenyl benzene)), and are written in shorthand here as poly(S-*r*-DIB), where “S” represents sulfur, “*r*” refers to the random nature of the binding, and DIB represents the aforementioned co-monomer. In general, this process affords statistical copolymers with randomized connectivity of sulfur and DIB co-monomer units, thus various concentrations of co-monomer may be included in the polymers.

Other co-monomers have since been utilized,^[21] as well as related creative methods for using molten sulfur.^[22] Overall this work has outlined several interesting possibilities for using polymers based on elemental sulfur in practical applications, including as a cathode in lithium-sulfur (Li-S) batteries, as copolymer films with tunable mechanical properties, and in the fabrication of infrared (IR) transmissive, high refractive index polymers.^[13,20] As a whole, this method points

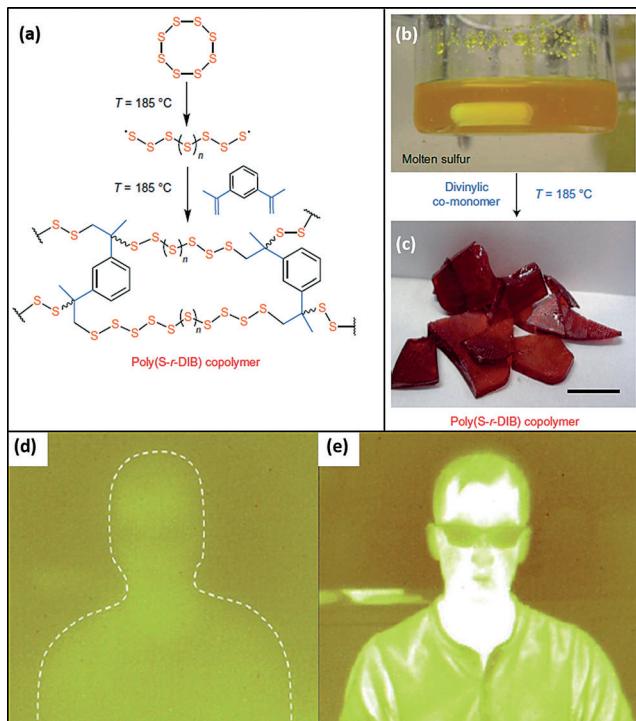


Figure 3. a) Synthesis through inverse vulcanization. b) An image of molten sulfur. c) The final poly(S-*r*-DIB) copolymer. Scale bar = 2 cm. d,e) A thermal image comparison of a human subject visualized through PMMA (d) and poly(S-*r*-DIB) (e) in the mid-wave IR region of the light spectrum (3–5 μ m). (a)–(c) Reproduced with permission from The Nature Publishing Group. Copyright 2013.^[13] (d) and (e) Reproduced with permission from the Wiley Publishing Group. Copyright 2014.^[20]

toward a very cheap, environmentally beneficial, and useful means by which to utilize the large stockpiles of elemental sulfur lining the fields of oil refineries across the planet (Figure 1).

One common practice for improving the optical properties of polymers is to incorporate sulfur either as pendant or backbone portions into the polymer.^[23] However, such polymers tend to contain high percentages of atoms that limit their use. Pyun and co-workers demonstrated that although polymers fabricated by inverse vulcanization appear red in color in the visible range of the light spectrum, they can be highly transmissive in the IR region, and can have refractive indices (*n*) that are unusually high for polymers (*n* > 1.80).^[20] These properties are attributed to their very high sulfur content. This makes such polymers superior to other polymers for visualization in the IR region (Figure 3). It has been further shown that, as a result of the dynamic nature of these polymers, damage caused to the surface (e.g. scratches) can be remedied by heating, thus restoring the desirable transmission capabilities.^[24] Given their properties, many opportunities exist for the use of these types of polymers in IR-optical applications.

Other research groups have worked to expand the possibilities of inverse vulcanization in the brief time since Pyun’s initial report. As sulfur itself is the solvent material in the inverse vulcanization process, much of the research has

focused on additives to molten sulfur that are stable at high temperatures, as well as the ability to either synthesize nanoparticles using sulfur as a copolymer^[26] or incorporate preformed nanoparticles into the polymer to alter the materials properties.^[25,27] Bear et al. demonstrated that several types of nanoparticles could be incorporated into poly(S-*r*-DIB) polymers, including gold nanoparticles, InP/ZnS quantum dots (QDs), iron oxide nanoparticles, and lead sulfide nanocrystals (Figure 4).^[25] The resulting sulfur-based

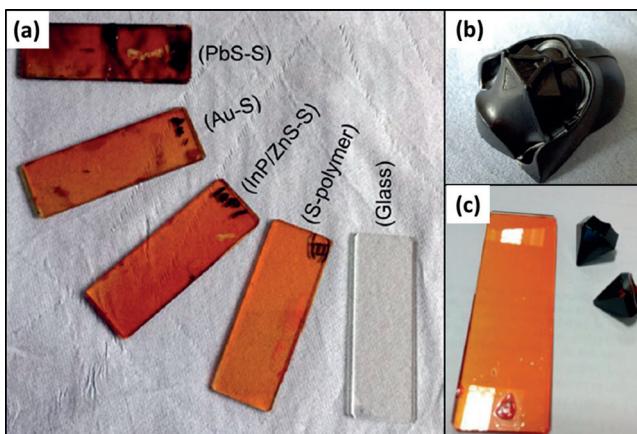


Figure 4. a) Thin films containing various nanoparticle types, and b) molded sulfur polymer containing Fe_3O_4 nanoparticles, all synthesized through inverse vulcanization. c) Similarly synthesized thin film and molded sulfur polymers devoid of nanoparticles. Reproduced with permission from The Royal Society of Chemistry. Copyright 2015.^[25]

polymers tended to express a color that was indicative of the type of nanoparticle incorporated; however, there were varying results with respect to the characteristic expression of each nanoparticle type within the sulfur-based nanocomposites. For example, the typical QD emission characteristics were quenched by the fabrication process of the QD nanocomposites, while characteristic surface plasmon resonances were observed for the sulfur-based nanocomposites that contained gold nanoparticles. Overall, the incorporation of nanoparticles into polymers through inverse vulcanization may lead to materials with further enhanced optical and mechanical properties.

Various co-monomer and pendant molecules have also been added to the inverse vulcanization process. Both 1,3-diethynylbenzene and 1,4-diphenylbutadiyne have been used in place of DIB as the co-monomer to bolster these sulfur-based polymers as viable cathode materials in Li-S batteries.^[28] 3,4-Propylenedioxythiophene was incorporated into the polymer matrix as a pendant linkage to the sulfur backbone to enhance the charge conductivity of the poly(S-*r*-DIB) polymers.^[21a] Finally, Pyun and co-workers utilized the inverse vulcanization method they established to produce nanocomposites of lead sulfide (PbS) nanoparticles with a high sulfur content.^[21b] In this process, oleylamine was used as the co-monomer with elemental sulfur, and the overall result was a method in which the *in situ* synthesized PbS nanoparticles could be precisely loaded and dispersed within the copolymer.

Recently, inverse vulcanization has been utilized in the production of dye-sensitized solar cells (DSSCs).^[29] Specifically, the authors employed polymeric sulfur, in the form of poly(S-*r*-DIB), as the hole transporting material in a DSSC. Interestingly, the method of polymer fabrication did not significantly deviate from the original poly(S-*r*-DIB) synthesis reported by Pyun and co-workers.^[13] Further research and optimization would certainly be required to make this process a viable alternative for the development of solid-state DSSCs. That said, the overall findings demonstrated that sulfur-based polymers made by inverse vulcanization could potentially be a low-cost, abundant source for hole-transport materials used in DSSCs.

Although inverse vulcanization is very much in its infancy, there are a multitude of applications in which this process may prove valuable to both the materials research field, as well as to the environment.

3. Sulfur in Rechargeable Batteries

With an operating voltage range of 2.1 Volts (V) and a theoretical capacity of 1675 milliamp hours per gram ($\text{mA}\text{h g}^{-1}$), sulfur (when combined with lithium) is superior in terms of safety and cost to other battery cathode materials currently being used in commercial applications.^[30] These facts, along with its semiconducting character and incredible abundance, have made sulfur a popular research focus for improving batteries. When combined with the Group 1 elements lithium or sodium, sulfur can be used to make batteries with desirable properties. Lithium-sulfur (Li-S) batteries, which have been known since the 1960s,^[31] have the potential to replace the prevalent lithium ion (Li^+) batteries which are used today in numerous devices including laptops, cell phones, and other portable display electronics. Sodium-sulfur (Na-S) batteries have also been studied for several decades and were once poised to become the industry standard for use in numerous applications.^[32] Although popularity in Na-S batteries decreased for several years because they were deemed too dangerous for broad use, some advances in technology and in fundamental understanding have spurred renewed interest in Na-S batteries for certain applications.^[33] This section focuses on Li-S and Na-S batteries, highlighting sulfur's increasingly important role in research on rechargeable batteries.

3.1. Lithium-Sulfur Batteries

Lithium is the lightest metal in the Periodic Table of elements, and it has the greatest energy density per unit weight of all the metals. Thus, it makes sense that lithium has been the focus of battery research for many years. Studies by Whittingham^[34] and Goodenough et al.^[35] brought Li^+ batteries into the forefront, and today Li^+ batteries are ubiquitous, largely replacing their rechargeable battery predecessors such as nickel-cadmium batteries. In general, the major goals of research in this area are to develop a rechargeable

battery type that is safe, low cost, and delivers a substantially increased battery lifetime and power.

Although ubiquitous, Li⁺ batteries are limited by several factors, including the need to maintain a constant charge (ca. 30% or greater) and the necessity of intercalation materials. A present-day rechargeable Li⁺ battery can typically provide a specific capacity of up to 200 mA h g⁻¹, with a cycle life between 300 and 1000 deep cycles (Table 1).^[36]

Table 1: Comparison of Li⁺ and Li-S cell characteristics. Adapted with permission from The Royal Society of Chemistry. Copyright 2013.^[36]

| Characteristic | Li ⁺ cells | Li-S cells |
|-----------------------------|------------------------------|-----------------------------|
| cell voltage | 3.4–4.0 V | 2.15 V |
| cathode specific capacity | 140–200 mA h g ⁻¹ | 1675 mA h g ⁻¹ |
| theoretical specific energy | 500–600 Wh kg ⁻¹ | 2600 Wh kg ⁻¹ |
| practical (obtainable) | 150–200 Wh kg ⁻¹ | 200–700 Wh kg ⁻¹ |
| specific energy | 1800 Wh L ⁻¹ | 2800 Wh L ⁻¹ |
| theoretical energy density | | |
| cycle life | 300–1000 deep cycles | < 200 cycles |

Although replacing the positive electrode materials currently used in Li⁺ batteries with sulfur decreases the battery cycle life to about 200 cycles, this is mitigated by the substantially greater (theoretical) specific capacity value of about 1675 mA h g⁻¹ for Li-S batteries (Table 1).^[30,31,36] Furthermore, the theoretical values for specific energy and energy density are both significantly greater for Li-S batteries (ca. 2600 and 2800, respectively) than those of Li⁺ batteries (ca. 550 and 1800, respectively).^[31,36] A major problem that needs to be addressed with sulfur cathodes in Li-S batteries is the formation of polysulfides, which hinder coulombic efficiency and lead to a drastic decrease in capacity.^[30] In general terms, the most efficient production at the cheapest cost is a major focus of Li-S battery research. Li-S research is such a hot topic^[37] that there have been numerous recent reviews covering it.^[38] Thus, just a few notable recent approaches toward improving Li-S battery performance and viability for the likelihood of mass implementation are presented below.

One intriguing approach to making viable Li-S batteries involves the aforementioned inverse vulcanization of elemental sulfur.^[13] Pyun and co-workers have published several studies in which they have demonstrated that the use of divinyl aromatic compounds to thermally bind opened sulfur rings leads to the resulting (mostly) sulfur solid retaining many of the characteristics of elemental sulfur.^[21a,28b,39] This means that most of the desirable electrochemical qualities of sulfur are maintained. By using poly(S-*r*-DIB) as the cathode material, Pyun and co-workers reported improved cathode capacities of greater than 800 mA h g⁻¹ in comparison to the 170 mA h g⁻¹ commonly seen with Li⁺ batteries.^[13] However, at 100 cycles, this capacity was shorter lived than Li⁺ batteries, which can typically cycle between 300 and 1000 times (Table 1). Further research into utilizing sulfur polymers prepared from inverse vulcanization demonstrated that the number of cycles could be improved by incorporating 1,4-diphenylbutadiyne as a co-monomer into the polymer, with

a cathode specific capacity of 800 mA h g⁻¹ obtained over about 300 cycles.^[28b] With a view to potential industrial implementation, a method for scaling up the production of these polymers for use in Li-S batteries has also been reported.^[39] Although further improvement of cycle life is necessary, this research is just one example of a promising approach that could lead to the development of viable Li-S batteries. This method has been used as a template for the development of other methods for making Li-S batteries by inverse vulcanization.^[40] As the process primarily uses elemental sulfur in its cathode material, this approach provides one means by which the abundant amounts of sulfur produced from oil refining can be beneficially utilized.

In another example that also uses a form of vulcanization, Park and co-workers reported the development of an organosulfur-based cathode for Li-S batteries that retains a capacity of 850 mA h g⁻¹ for 450 cycles, with a 99% coulombic efficiency.^[41] This approach is based on the development of organosulfur compounds from elemental sulfur. These compounds were synthesized using “soft templates” made up of trithiocyanuric acid (TTCA) crystals. Sulfur was embedded into the porous TTCA templates during two vulcanization steps, after which cross-links were formed between the elemental sulfur and TTCA (Figure 5). By using this process, it was possible to control the shape and morphology of the final organosulfur product. Perhaps most importantly, the amine groups of TTCA aided in the fast transport of lithium ions during battery cycling. Overall, this method allowed organized lithium ion coordination sites to develop, and these sites were critical for the transport of lithium ions into the active materials.

A typical Li-S cell contains the active sulfur material, a carbon additive, and a polymer binder.^[42] Most of the published research tends to focus on the sulfur and carbon components, but a different approach to developing viable Li-S batteries would involve adjusting the binder material. Zhang and co-workers demonstrated that the performance of Li-S batteries could indeed be improved by altering the polymer binder material.^[42] By using this approach, the authors described a Li-S battery system that maintained a capacity of about 840 mA h g⁻¹ for 500 cycles. To accomplish this feat, they used Gum Arabic (GA) as the polymer binder to improve the battery cyclability. GA was chosen because it has beneficial mechanical properties, and because it contains functional groups that aid in decreasing polysulfide shuttling. An additional benefit in using GA, which derives from the *Acacia Senegal* tree, is that the GA polymer binder source is sustainable. It should be noted that unlike many other published examples of Li-S batteries in which the capacity shows a substantial steady decrease, or decreases greatly after a certain number of cycles, the capacity of the Li-S battery using GA as the binder was remarkably stable throughout.^[42]

Although many researchers are optimistic about the prospect of Li-S batteries replacing Li⁺ batteries as a lighter and safer energy material, some remain skeptical. Hagen, et al. recently published an extensive statistical and comparative report in which they concluded that expectations of the Li-S system as a Li⁺ battery replacement are too high and perhaps overrated.^[43] Similarly, Rosenman, et al. also cau-

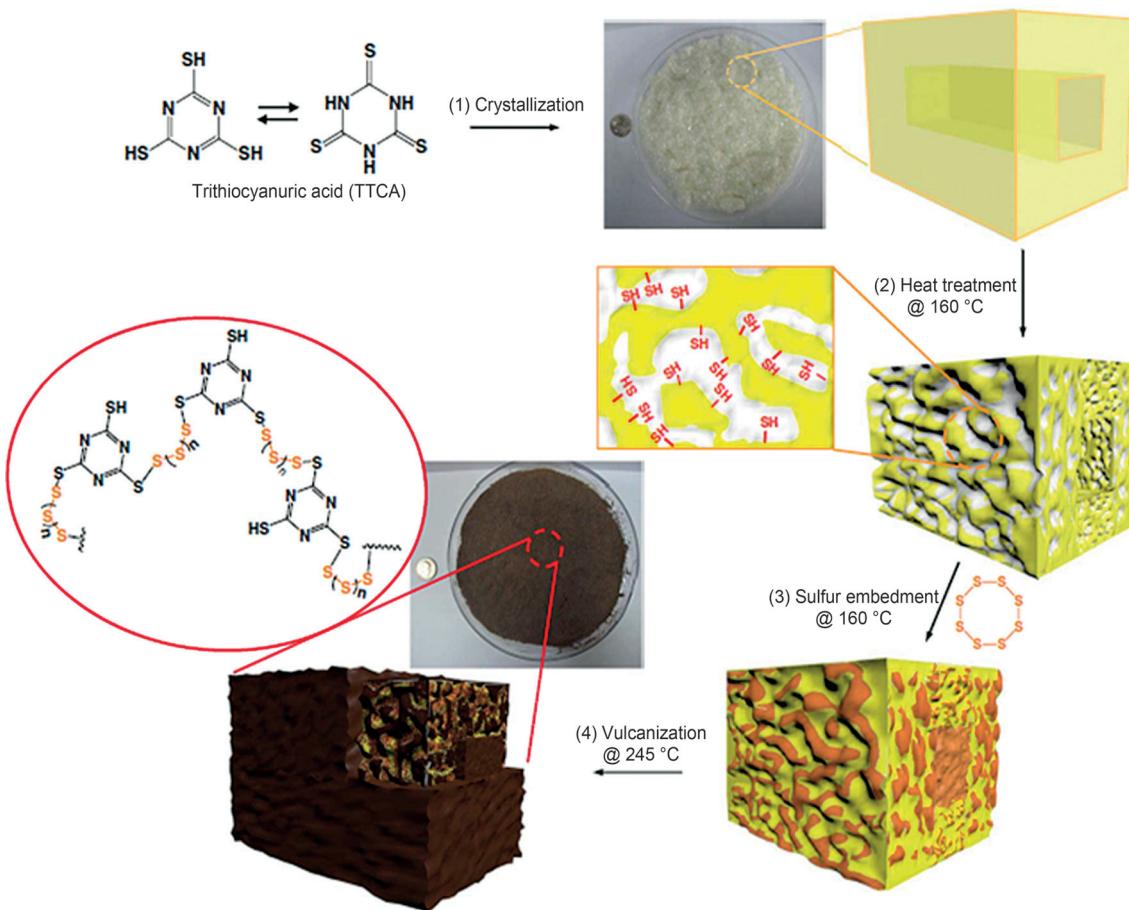


Figure 5. Synthesis of sulfur-rich polymers for use in Li-S battery cathodes. Reproduced with permission from The Nature Publishing Group. Copyright 2015.^[41]

tioned that many research reports on Li-S batteries are not practically sound in terms of industrial production and product implementation.^[44] Furthermore, both sides of the debate point to the shuttling of polysulfides as a major problem that must be addressed before Li-S batteries can truly be used in everyday applications. Regardless of whether or not the current research buzz surrounding Li-S batteries will lead to implementable systems, there is definitely a need to replace Li⁺ batteries with a safer battery system that offers more power at safer operating voltages and cheaper production costs. It is important to recognize that Li-S batteries may not be that system, but research in this area will likely provide the knowledge and understanding to develop such a system. Perhaps combining improvements in each of the Li-S cell components (i.e. the active sulfur material, the conductive carbon additive, and the polymeric binder), as opposed to focusing merely on one cell component, is a route that should be pursued for those seeking to replace current battery technologies with Li-S batteries.

3.2. Sodium-Sulfur Batteries

Although not nearly as popular as a current research topic, there is interest in using Na-S as the cathode material

for batteries in certain applications because Na-S provides some clear advantages as an electrode material. For example, whereas Li-S batteries have to remain at least 30 % charged at all times, Na-S batteries do not have to maintain a charge at all. Other advantages include the long-cycle life and high energy density. As a result, Na-S batteries are currently used in several countries for the storage of electrical power that is produced by wind power, photovoltaic devices, as well as for conventional power plants.^[45]

Finally, Na-S batteries are considered by some to be environmentally benign because they do not produce emissions while in use (because of their seals) and nearly all of the battery materials can be recycled.^[46] Given the many advantages, Na-S batteries are proving to be a valuable research topic in this era in which we seek alternative energy sources.

One of the major challenges that faces the implementation of Na-S batteries is that in order to fully take advantage of its high conductivity, the batteries must operate at high temperatures (ca. 300 °C) so that the electrode materials maintain a molten state (Figure 6). Consequently, there needs to be an adequate seal in place that can function at the high temperature without cracking. For this purpose, Song, et al. have developed several glass ceramic sealant materials.^[47] They used borosilicate as the basic glass component, and added various other components, such as Y₂O₃ and CaF₂, to modulate the

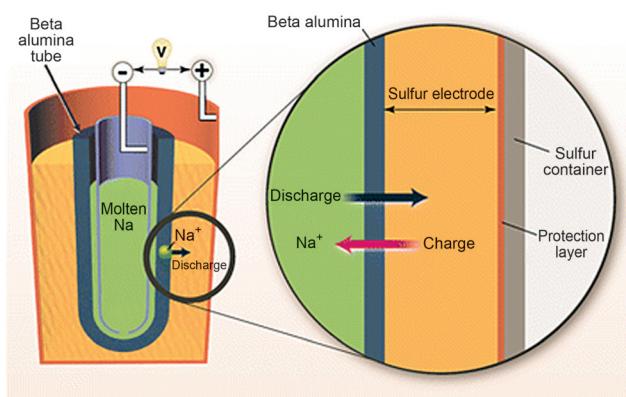


Figure 6. Principle of a Na-S battery. Reproduced with permission from AAAS Publishing. Copyright 2011.^[45b]

thermal expansion coefficient of the sealant, while decreasing its viscosity. These components were melted together, then cooled and ground into powders. The powders were shaped into cylinders and placed between alumina plates, heated at 350°C for 60 minutes, then rapidly cooled to room temperature. This process, which was cycled 100 times, was carried out to determine the sealant behavior under shock conditions. This work ultimately resulted in several ceramic sealants that could withstand the temperature and compatibility demands of the typical Na-S battery setup under shock conditions, thus proving useful for safe storage and the operation of Na-S batteries in industrial applications.^[47]

Of course, Na-S batteries would be more desirable if their advantageous properties could be accessed at lower temperatures.^[48] Recently, there have been a number of reports detailing efforts to produce Na-S batteries that not only function at decreased temperatures, but specifically at room temperature.^[49] Perhaps most notable are the studies by Yu and Manthiram, who have detailed novel approaches to developing room-temperature Na-S batteries.^[50] In one such report, the authors offered a kinetic rationale for maintaining long-chain sodium polysulfides in the cell so as to maintain high capacity during cycling. To achieve this, they prevented polysulfide migration from the cathode to the anode by partitioning the polysulfides using a carbon nanofoam interlayer. By using this approach they were able to make a reversible, room-temperature Na-S battery system with an energy density output of 450 Wh kg⁻¹ at a cost of \$10 per kilowatt hour.^[50b] Although the specific capacities of the Na-S batteries reported were not as good as those reported for Li-S batteries, the cost-performance ratio of the Na-S batteries are more favorable than that of traditional Li⁺ or Li-S batteries.^[50b] Having already demonstrated value as an energy grid storage material, further studies to improve and make Na-S batteries more accessible are certainly warranted.

Whether being used in combination with lithium or with sodium, sulfur's ability to bind with other atoms and molecules, its inherent energy properties, and its tremendous abundance have made sulfur an advantageous tool in searching for improved, safer, and more environmentally friendly power sources for the future.

4. Thiol Coupling Reactions

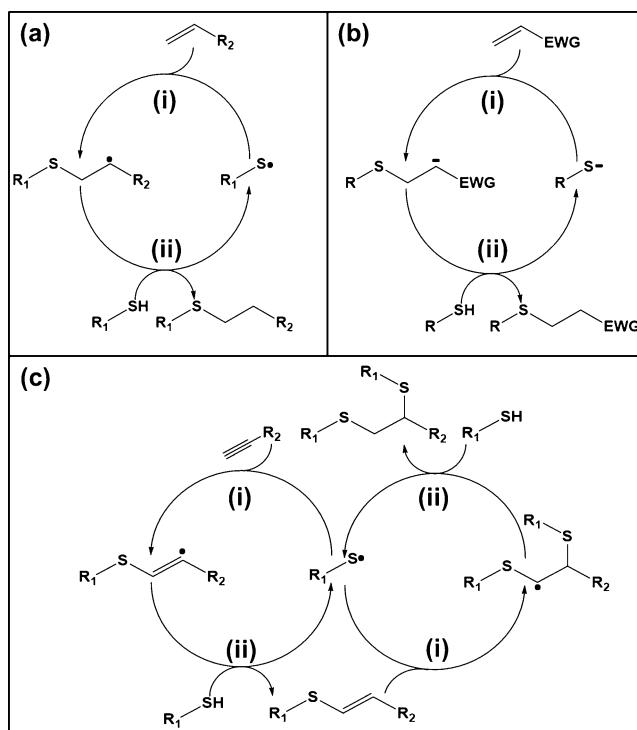
A major research area that has emerged in the past decade falls under the umbrella term thiol click chemistry.^[51] Although some of these reactions have been known for more than a century,^[52] there has been a renaissance in the use of thiol click reactions, a research area that was extensively developed by the group of Charles Hoyle, as well as other groups. Thiol click chemistry is often included as a subset of the click chemistry family,^[53] even though some of the reactions do not truly fit the rigorous parameters of the click concept.^[54] Nevertheless, these reactions tend to be quite efficient “coupling” reactions, and thus incredibly useful. For the purposes of this Review, this family of reactions will be termed “thiol coupling.”

In general, thiol coupling reactions are anti-Markovnikov addition reactions that can be initiated thermally, by radical initiators, or by photoinitiation. For example, a single “ene” group can react to form a bond with a thiy radical group that was formed upon initiation. In the case of thiol-yne reactions, a single “yne” group can react to form bonds with two thiyl radicals.^[51a,55] A principle advantage of thiol coupling reactions is their generally successful performance in air, with virtually no inhibition by oxygen, which is a common problem for numerous other polymerization reactions. Important reactions included in the family of thiol coupling are thiol-ene, thiol-yne, and thiol-Michael addition (Scheme 1). As there have been several useful comprehensive reviews focused on thiol coupling published in the past few years,^[51,56] this section will outline just some of the materials that have been produced from these reactions, and the interesting ways in which these sulfur-based reactions were used to make them.

4.1. Nanocomposites

Developing multifunctional nanocomposites with beneficial mechanical and optical properties by thiol coupling reactions is an area that is of particular interest to many materials scientists. In a 2008 publication, Hoyle and co-workers developed a method for incorporating “bare” gold nanoparticles (AuNPs) into a thiol-ene matrix.^[57] Mechanical analysis of the thiol-ene nanocomposites indicated an increase in the glass transition temperature, but a decrease in the degradation onset temperature as the AuNP concentration increased. Perhaps most significant, however, was that thin films of the thiol-ene nanocomposites were transparent, even at the greatest AuNP concentration studied.

Building upon that study, the Ligler research group at the US Naval Research Laboratory (NRL) developed a method for incorporating both gold and silver nanoparticles into thiol-ene and thiol-yne polymer matrices by UV polymerization.^[58] In contrast to the work by Hoyle and co-workers, the Ligler group functionalized the NPs with ligands functionalized at both ends. These ligands were surface-bound to the NPs through a thiol group on one end, and could cross-link with the polymer matrix through vinyl or alkynyl groups on the opposite end (Figure 7).



Scheme 1. Proposed reaction cycles for the a) thiol-ene addition, b) thiol-Michael addition, and c) thiol-yne addition, where (i) represents a propagation step and (ii) represents a chain transfer step. R₁ and R₂ are substituent groups, and EWG represents an electron-withdrawing group. Adapted with permission from The Royal Society of Chemistry. Copyright 2010.^[51a]

Although the same general trends in optical and mechanical properties were observed when comparing their thiol-ene nanocomposites with those of Hoyle and co-workers, the method employed by Ligler and co-workers drastically decreased the time in which such nanocomposites could be fabricated from days and weeks down to minutes. This approach was the first to produce thiol-yne nanocomposites, and the thiol-yne nanocomposites showed different properties in some respects from those of the thiol-ene nanocomposites. For example, the T_g values of the thiol-ene nanocomposites steadily increased as the nanoparticle concentration increased starting from native thiol-ene, but none of the T_g values determined for the thiol-yne nanocomposites were as high as the T_g value of 47°C determined for the native thiol-yne polymer. All of the T_g values determined for the thiol-yne nanocomposites were much higher than those of any of the thiol-ene nanocomposites. The likely reason for this is the additional π bond that exists in the thiol-yne nanocomposites than in the thiol-ene reactions, which affects the kinetics.^[60] One key finding of this study was that the ligand bound to the NP surface within the nanocomposites has an impact on the distribution of the NPs within the polymer, and the surface-bound ligands also affect the color of the final material.^[58] This conclusion agrees with an earlier report by Lee and Bowman that indicated that functionalizing nanoparticles and subsequently incorporating them into thiol-ene polymers has an effect on the kinetics and thus the properties of the resulting materials.^[61] In a follow-up study, Ligler and

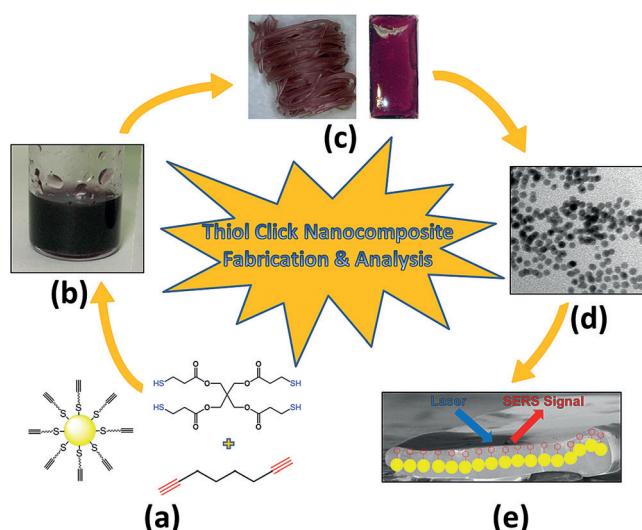


Figure 7. a) Reagents for preparing thiol-yne nanocomposites. b) Pre-polymer solution containing thiol-yne reagents and functionalized nanoparticles. c) Representative thiol-yne nanocomposite fibers (left) and film (right) fabricated by photopolymerization of the pre-polymer solution. d) Representative TEM image of gold nanoparticles within a thiol-yne nanocomposite film. e) Schematic representation highlighting the ability to detect gold nanoparticle surface molecules within thiol-yne nanocomposites by surface-enhanced Raman spectroscopy.^[58,59]

co-workers were also able to show that surface-enhanced Raman spectroscopy (SERS) could identify specific molecules attached to the surfaces of the incorporated NPs within the porous versions of these nanocomposites.^[59]

4.2. Optically Active Materials from Thiol Coupling Reactions

As sulfur allows for transmission in the infrared region of the light spectrum, is well known to increase the refractive index of materials, and readily binds to various surfaces (e.g. metallic nanoparticles), thiol coupling reactions are often employed to develop materials for optical purposes. As a result, there have been numerous reports of using thiol coupling to incorporate liquid crystals for optical and actuation purposes.^[62] One such example involves the development of gold nanorods (AuNRs) containing liquid-crystal elastomers that respond to near-infrared (NIR) light.^[63] The authors pointed out that the localized surface plasmon resonances of AuNRs can be tuned to the NIR region. Elastomers that contain both AuNRs and liquid crystals could then be developed to specifically respond to NIR light. NIR-responsive liquid-crystal elastomer fibers were formed by using a sequence of three thiol-ene reactions that included incorporating the AuNRs into the elastomer matrix. The alignment of the liquid crystals was studied by polarized optical microscopy and the results showed uniformity of alignment. Perhaps most importantly, the fibers were shown to shrink and expand in response to the presence or absence of NIR light on a timescale of hours, thus demonstrating the

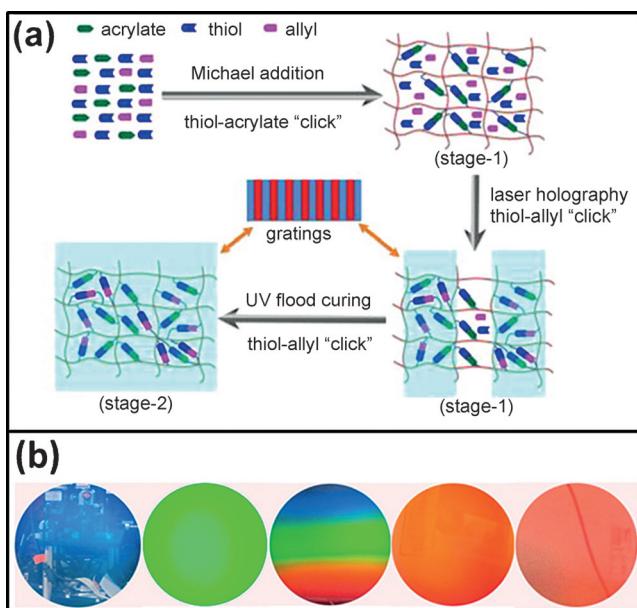


Figure 8. a) Schematic representation of holography by two-stage orthogonal thiol-click chemistry, and b) the resulting graded rainbow holograms. Reproduced with permission from The American Chemical Society. Copyright 2014.^[65]

potential for the development of actuating materials using this method.

Another way in which thiol coupling reactions are being utilized in optical applications is through the development of holographic polymers.^[62a, 64] In a carefully carried out study, Bowman and co-workers developed graded, rainbow-colored holograms through orthogonal thiol coupling reactions (Figure 8).^[65] The beauty of using orthogonal reactions is that specific reactants can be activated at desired steps within a complex series of reactions given the proper stimulus. In this case, a patterned substrate was first developed through thiol-acrylate Michael addition. This step established a template backbone from which to perform further reactions by controlling the thiol, acrylate, and allyl stoichiometries. The subsequent steps involved activating the available unreacted thiol and allyl groups (thiol-allyl coupling) through irradiation with UV light. The end result was a blue-to-red, rainbow-colored hologram with high modulus, high refractive index, and a high glass transition temperature (Figure 8).

The facile development of complex holograms as described could prove incredibly valuable in applications including three-dimensional display development and anti-counterfeiting measures.

4.3. Sensing and Separations through Surface Modifications

Since sulfur is a common linker for surface attachment, thiol coupling reactions are frequently used to modify the surfaces of materials to impart specific properties and/or characteristics to those surfaces. Consequently, this means thiols can be used in sensing applications through surface attachment. This was demonstrated in the previously mentioned SERS analysis of thiol-yne nanocomposites,^[59] and also

by the modification of the surfaces of thiol-yne fibers.^[66] One of the best known examples of surface modification by thiol coupling reactions originated from the Patton research group. In conjunction with photolithography, sequential steps of photoinitiated thiol-yne reactions were used to generate surfaces with specific hydrophilic and hydrophobic regions.^[67] Although this was a simple demonstration of the power of photoinitiated thiol-yne reactions, broader valuable aspects of this study include the ability to perform thiol coupling reactions under mild and easily accessible conditions (e.g., under mere sunlight), and the orthogonality that the arsenal of thiol coupling reactions brings to bear.

Several research groups have developed hybrid porous monolithic columns (HPMCs), often in conjunction with polyhedral oligomeric silsesquioxanes (POSS), to detect small molecules through thiol coupling reactions.^[56c, 69] HPMCs are a relatively recent invention for purification and separation that allows for the fast separation of specific targets with a high flow rate and high-throughput capability.^[70] Facile fabrication of such columns is an incredibly valuable asset, and one that favors fabrication by using the various thiol coupling reactions, as demonstrated by the work of Zou and co-workers. By using various thiol coupling reactions—including thiol-epoxy,^[71] thiol-acrylate,^[72] thiol-Michael,^[73] photoinitiated thiol-ene,^[74] and photoinitiated thiol-yne reactions^[68]—Zou and co-workers have developed HPMCs with high column efficiencies (Figure 9). In each case the HPMCs demonstrated significant chemical, thermal, and mechanical stability, further demonstrating their practical viability as chromatography columns. As the starting materials are cheap, readily available, and the HPMCs are quite efficient, it is conceivable that thiol coupling reactions may play an important role in future technologies for the separation of small molecules.

4.4. Modification of Carbon-Based Nanomaterials

The discovery of Buckminsterfullerene (C_{60}) in the 1980s,^[75] the re-emergence and intense study of carbon nanotubes in the 1990s,^[76] and the explicit outlining of graphene fabrication and properties in the 2000s^[77] led to extensive research being carried out on nanoscale carbon materials by researchers in the physical sciences all around the world. These molecules are of interest because of their size, their electronic capabilities, and their potential for use in applications such as energy and optics. Surface modification of the various types of nanoscale carbon molecules for the development of electronically interesting materials is a popular avenue of research. Several research groups have used thiol coupling reactions as a means to further explore the modification of nanoscale carbon molecules, including fullerenes^[78] and graphene.^[79]

Yagci and co-workers were among the first to functionalize C_{60} through thiol-ene reactions. The C_{60} derivatives obtained were capable of undergoing further modifications that allowed for polystyrene to be grafted onto C_{60} .^[78a] Inspired by this, Mazzier et al. developed polypeptide polymers that were end-capped with C_{60} by using a thermally

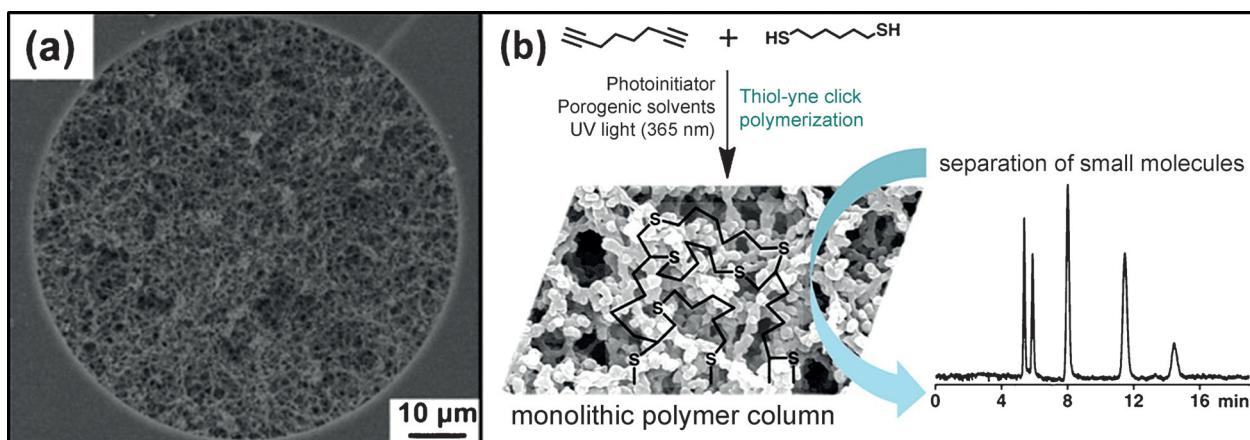


Figure 9. a) Cross-section image of a polymer monolith. b) Scheme showing the components and conditions for the preparation of columns, as well as representative elution data for the separation of small molecules. Reproduced with permission from The American Chemical Society. Copyright 2014.^[68]

initiated thiol-ene reaction.^[80] The resulting polymers were found to self-assemble in water into rodlike microstructures that had C₆₀ on either their N or C terminus. The goal of this work was to impart photophysical and/or electrochemical functionalities to polypeptide microstructures, as well as to outline a route for the large-scale production of fullerene-based devices. Ultimately, this study demonstrated that, by taking advantage of the ease and simplicity of thiol-ene reactions, the possibility of imparting such functionalities is indeed possible.

Salavagione and co-workers have outlined a method for functionalizing the surface of graphene and graphene derivatives through thiol-ene and thiol-yne reactions.^[78c,81] Although there are many methods of functionalizing graphene (including CuAAC click reactions), the functionalization of graphene by thiol coupling reactions is often particularly facile because the reactions do not require rigorous precursor steps or catalysts such as copper. To determine the best means to functionalize graphene through click chemistry, a comprehensive comparison of graphene modification through CuAAC click, thiol-ene, and thiol-yne reactions was performed by functionalizing graphene with short-chain polyethylene (Figure 10).^[81] It was determined that the resulting properties of the graphene were dependent on the method used to modify the graphene. Thiol-ene reactions were ultimately determined to be the most desirable method for the surface functionalization of graphene as the properties of the modified graphene were superior to those obtained using either thiol-yne or CuAAC click reactions.^[81]

4.5. Organometallic Coupling Reactions

One of the most beneficial aspects of thiol-coupling reactions is the ability to “click-in” functionality by merely changing the molecule housed between (or appended to) polythiols, polyvinyls, polyalkynyls, or multifunctional molecules containing at least 1 thiol functionality and at least 1 other functional end group. With this in mind, one area that has not been as heavily explored is the incorporation of

inorganic molecules with known useful properties. One such molecule is the electrochemically active sandwich compound ferrocene. By synthesizing organometallic molecules such as ferrocene to be “thiol-clickable”, opportunities exist to develop materials with improved optical, electrochemical, and mechanical properties.^[82]

The Manners group has investigated the preparation of organometallic compounds for many years, including recent forays into using thiol-coupling reactions to develop poly-ferrocenyl homopolymers with silane linkages.^[84] Recently, the Cuadrado research group also utilized thiol-ene^[85] and thiol-yne^[83] reactions to incorporate ferrocene as backbone, pendant, or peripheral molecules into polymer films with and without silane connecting groups (Figure 11). In addition to presenting various ways to incorporate ferrocene, these reports also outline the electrochemical aspects of the materials produced. In general, the polymers retain much of the very desirable electrochemical activity of ferrocene. Furthermore, the authors demonstrated that the thiol-coupling reactions used to make these electroactive polymers could be carried out by using heat or photoinitiation. In contrast to the two-step coupling process typical of thiol-yne reactions, the use of ethynylferrocene as a starting component did not lead to double hydrothiolation under any of the conditions studied, but instead resulted in sulfur-bridged ferrocenylvinyl moieties.^[83] This suggests that orthogonal reactions could perhaps be used for further coupling at these bonds. Ultimately the simplicity of the process to develop novel compounds that retain the properties of their precursors could conceivably be applied to various other organic and inorganic molecules with known electroactive and/or optical properties.

4.6. Fabrication of Functional Materials through Microfluidics

Microfluidics and the concept of “lab-on-a-chip” analysis continues to be an important focus of analytical chemistry because of the small scale of the components used, the potential for decreased costs for implementation, and the

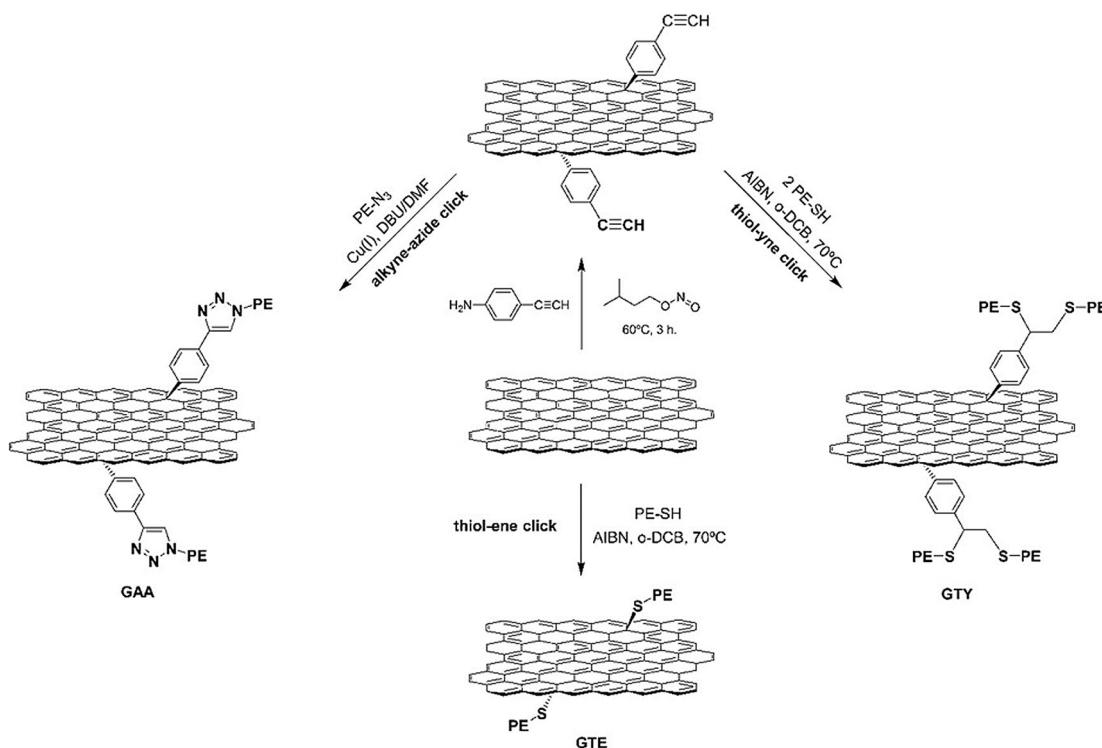


Figure 10. Graphene modification through CuACC click, thiol-ene, and thiol-yne reactions. Reproduced with permission from The American Chemical Society. Copyright 2013.^[78b]

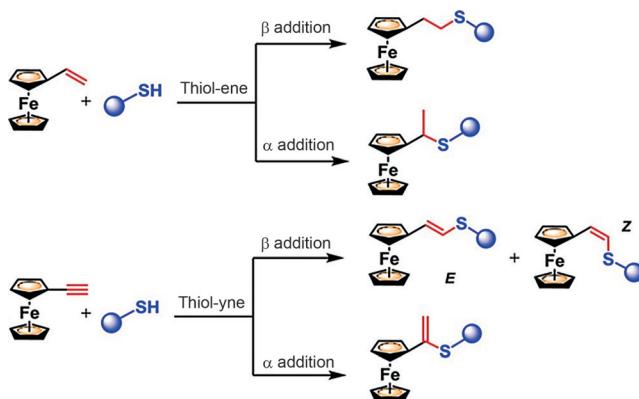


Figure 11. Schematic representation showing the modification of ferrocene through thiol-ene and thiol-yne reactions with the resulting possible addition products. Reproduced with permission from The American Chemical Society. Copyright 2014.^[83]

purported high sensitivity.^[86] Microfluidic research is also fast-becoming a focal point of research in materials science.^[87] Thiol-coupling reactions have been used extensively in microfluidics research to produce materials as diverse as functional polymer beads,^[88] microactuators,^[62e] fibers with noncircular cross-sections,^[66,89] anisotropic microparticles,^[90] sensing conduits,^[56c] soft lithography microstructures,^[91] hydrogels,^[92] waveguides,^[93] and even to make microfluidic channels themselves.^[94]

Perhaps one of the most significant outgrowths of microfluidic research that utilizes thiol coupling reactions came from that last example.^[94] Carlborg et al. used nonstoichio-

metric ratios of alkenes to thiols to make microfluidic channels. They termed this methodology off-stoichiometry thiol-ene chemistry (OSTE). By using OSTE, the authors were able to tune the mechanical properties of the thiol-ene microfluidic channel that was fabricated, and they were also able to precisely seal the channel through direct UV bonding. Building on the OSTE concept, a much broader adoption of OSTE to develop materials with capabilities for post-polymerization modification has since been used by other research groups for various purposes, including extending the concept to off-stoichiometry thiol-yne chemistry (OSTY).^[56c,66,95] Although OSTE necessarily violates the “stoichiometric components” concept of click chemistry, this method can be incredibly valuable when one desires to perform post-polymerization modifications.

During the last decade, Ligler and co-workers expanded an interest in hydrodynamic focusing from applications in flow cytometry and microfluidic biosensors^[86a,87,96] to the fabrication of polymer microfibers by casting or photopolymerization.^[97] By using specifically designed microfluidic chips, fibers could be produced in a continuous fashion and both the shape and the size of the microfibers could be precisely controlled.^[89a] Building on studies on the production of acrylate fibers by photopolymerization,^[98] photoinitiated thiol-ene and thiol-yne reactions were used to fabricate fibers of various shapes and sizes, including round, hollow, “ribbon-shaped,” and “double-anchor” shaped fibers (Figure 12).^[66,89] Other shapes, which are also likely achievable using thiol coupling reactions, have been subsequently demonstrated using other reactions and similar microfluidic devices.^[99] Wicking, cell transport, and interlocking capabilities can be

imparted to the fibers depending on the shape of the fibers produced.^[89] A major advantage of using photoinitiated thiol-coupling reactions is the possibility of performing post-polymerization modifications using the aforementioned OSTY/OSTY concept. Using OSTY, Boyd, Ligler, and co-workers demonstrated that it is possible to carry out surface reactions by attaching a biotin-tagged maleimide to the excess thiols on the surface of polymerized fibers, followed by the attachment of fluorescent-tagged streptavidin.^[66] By using controls for nonspecific binding and autofluorescence, it was determined that the surface reactions were specific for the excess thiols, thus indicating the possibility of using OSTY materials in sensing applications (Figure 12).

Although microfluidics was the method of fabrication used to produce fibers in the studies by Ligler and co-workers, it should be noted that the production of thiol-ene fibers has been demonstrated using other fiber fabrication methods.^[100] Notably Ellison and co-workers have demonstrated methods for fabricating thiol-ene fibers using electrospinning,^[101] including a biorenewable fabrication of fibers based on soybean oil.^[101,102]

4.7. Biological Materials from Thiol Coupling Reactions

There are many ways in which thiol-coupling reactions have been implemented for biological purposes. Biological

applications of thiol coupling reactions include the development of bio-based telechelics,^[104] protein-conjugated/temperature-responsive polymers,^[105] self-healing polymers,^[106] and functionalized nanoparticles for targeted drug delivery.^[106] This section briefly addresses a couple of the more extensively researched ways in which thiol coupling reactions have been used for biologically relevant purposes.

Hydrogels, which are hydrophilic polymer networks that can swell tremendously with the introduction of water, can be fabricated using thiol coupling reactions.^[107] Thus far, the principle applications for these hydrogels tend to be biological in nature including cell encapsulation,^[108] tissue engineering,^[92] self-healing,^[106] and drug delivery.^[109] The Anseth group has been a leader in utilizing thiol coupling reactions to develop biologically useful hydrogels, including enzyme-responsive degradable hydrogels,^[110] cyocompatible/dynamically tunable hydrogels,^[111] and human stem cells encapsulated in cell-degradable hydrogels.^[112] In one of the earlier publications from the Anseth group on this topic, hydrogels were fabricated through thiol-norbornene reactions (Figure 13).^[113] In this study, cells that were encapsulated by the hydrogels remained viable throughout the processing of the material, and were also accessible for manipulation within the hydrogels after fabrication of the hydrogel. Two of several noteworthy aspects of this study were the use of photo-initiation, which did minimal harm to the cell viability, and the use of thiol groups from cysteine residues as the hydrogel

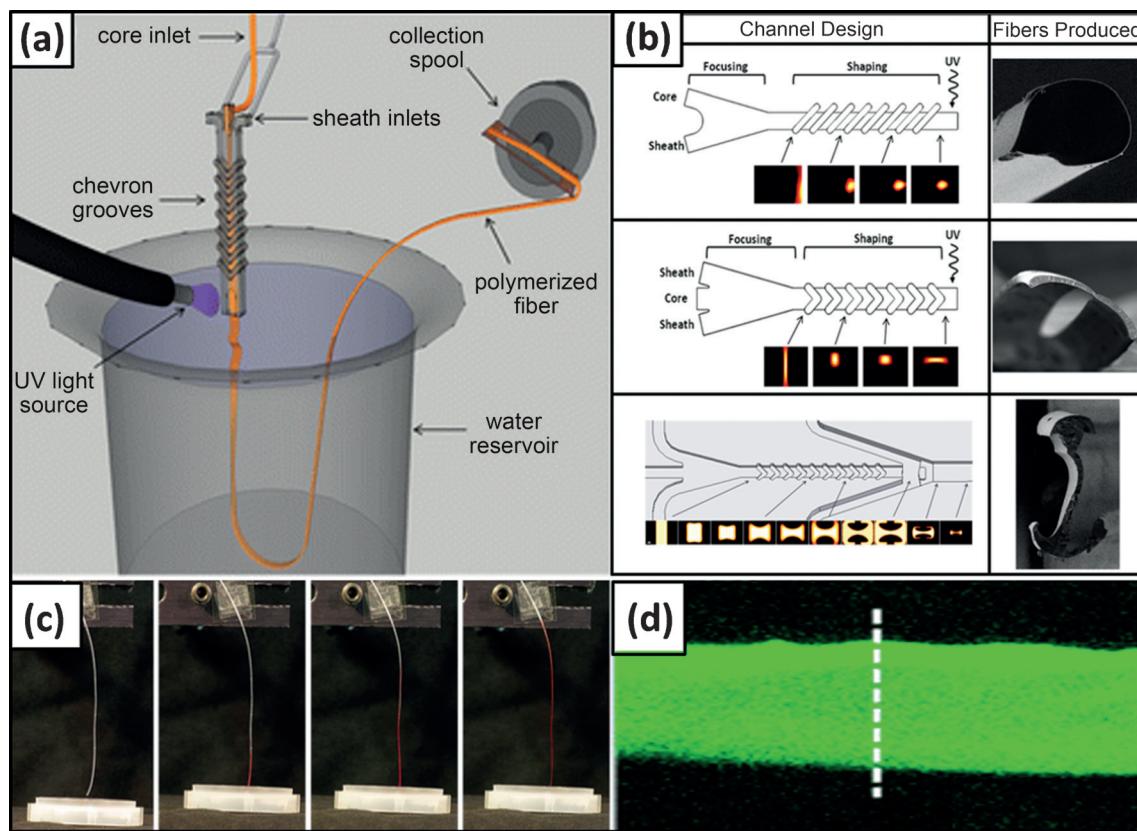


Figure 12. a) Microfluidic setup for the fabrication of fibers. b) Examples of microfluidic channel designs with snapshots from the COMSOL simulations used to design them, and the resulting fiber cross-section shapes. c) Time-elapsed images showing the wicking of red dye fluid traveling up a double-anchor shaped fiber. d) Image indicating the attachment of a fluorescent tag to surface thiols on a ribbon-shaped fiber prepared by off-stoichiometry thiol-yne (OSTY) chemistry.^[66,89b]

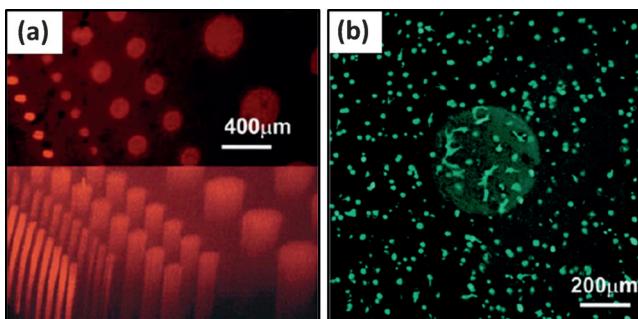


Figure 13. a) 3D projection images of photopatterned peptide cylinders in a hydrogel. b) 3D projection image of cells within a degradable hydrogel. Reproduced with permission from the Wiley Publishing Group. Copyright 2008.^[113]

cross-linking sites, thereby eliminating the need for post-synthetic modification. The viability of the cells, the simplicity of the hydrogel fabrication, and the ease with which the components were tailored for specific purposes demonstrated the effectiveness of thiol coupling reactions in research focused on biological mimics.

In perhaps one of the more practical uses for thiol coupling reactions, Bowman and co-workers have published several reports on the use of thiol-ene reactions in dental restorative materials.^[114] This study addresses the need for an alternative to the traditional amalgam tooth fillings and modern polymer resins that need to be replaced with great frequency. Improved nonmetallic polymer dental resins need to be decay-resistant, conformable, nontoxic, easy to insert, and have high mechanical strength. Each of these requirements can be achieved by using photoinitiated thiol coupling reactions. A major advantage of using thiol-ene resins is that, in addition to avoiding oxygen inhibition, they do not experience the extensive shrinkage seen in other polymer resins upon polymerization. Extensions of the initial work also showed that combining thiol-ene systems with methacrylate systems can further decrease shrinkage while maintaining the advantageous properties of both the thiol-ene and methacrylate resin systems.^[115] Finally, by using thiol-norbornene reactions, it has been shown that the glass transition temperature of the resulting polymer can be dramatically increased ($> 90^\circ\text{C}$), thus implying other ways in which thiol coupling reactions can be used to improve dental restorative materials.^[116]

Overall, it is clear that the sulfur-based set of reactions that comprise the family of thiol coupling reactions is both exceptionally versatile as well as tremendously useful. As thiols are common to many naturally occurring and synthetically derived molecules, thiol coupling reactions are readily taken advantage of. Although this set of reactions has found utility in applications ranging from medicine to optics and nanotechnology to separation science, the vast untapped possibilities for its use in the future are innumerable. Suffice it to say, research focused on thiol coupling reactions is poised for further exploration and implementation, and these reactions represent a major way in which sulfur will play a role in modern materials science.

5. Summary and Outlook

Sulfur is a key element in life on Earth, and it is proving to be a major focus for a wide range of research scientists. The broad interest in sulfur as a research focus is evident from recent reports of reforms to vulcanization processes, the need for improved battery systems, and emerging uses for thiol coupling reactions, as specifically addressed in this Review.

In addition to novel attempts at making rubber recyclable through inventive updates to traditional vulcanization methods, inverse vulcanization is an innovative means by which the large stores of excess sulfur on Earth can be utilized for beneficial purposes. As discussed, the growing list of materials formed through inverse vulcanization includes IR-transmissive optical lenses, dye-sensitized solar cells, and cathodes for lithium-sulfur batteries.

As a consequence of its advantageous intrinsic properties, sulfur can combine with either lithium or sodium for use as a key component in rechargeable batteries. The benefit in using sulfur in this way is that this may lead to cheaper, safer, and more powerful rechargeable batteries when combined with lithium, or powerful energy storage conduits when combined with sodium. Both battery types have their merits as we seek more efficient and environmentally beneficial energy alternatives.

The importance of sulfur in modern materials science is further exemplified through the extensive usage of thiol coupling reactions. Besides the examples of thiol coupling reactions highlighted in this Review, many others exist, including dendrimer synthesis,^[117] POSS fabrication,^[118,119] electroluminescent networks,^[120] surface chemistry,^[62c,100,121] and creative materials for reaction catalysis.^[122] Indeed, a book was recently written exploring many of these thiol coupling processes and products.^[123]

Overall, sulfur is a major player in an expansive area of exciting research taking place in modern materials science. This Review was not meant to be exhaustive in its investigation of sulfur, and it is important to note that there are many other ways in which sulfur is being implemented and utilized for environmental and energy-focused purposes in materials science.^[124] This includes research on biologically based materials, especially those focused on DNA sensing^[125] and cysteine modifications.^[126] Additionally, research involving materials that have implications in energy and electronics further demonstrate sulfur's prominence and popularity in current research; such research includes (semi)conducting materials such as (poly)thiophenes,^[12] molybdenum disulfide,^[11] and quantum dots.^[127] A similar report could also be written about the other chalcogens selenium and tellurium, and how they are often used in similar ways as (and in conjunction with) sulfur.^[128] However, sulfur stands at the forefront of these related atoms, and this fascinating element has a strong and increasingly prominent role to play in modern materials science and the general improvement of our lives.

Acknowledgements

This work was supported by the Jerome and Isabella Karle Fellowship, the Naval Research Laboratory, and the Optical Materials and Devices Branch of the Optical Sciences Division at the NRL through the Karle Fellowship. The views in this Review are those of the author and do not represent the opinion or policy of the US Navy or Department of Defense.

How to cite: *Angew. Chem. Int. Ed.* **2016**, *55*, 15486–15502
Angew. Chem. **2016**, *128*, 15712–15729

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Received: May 11, 2016

Published online: November 8, 2016