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Sulfur Chemistry

Elemental Sulfur as a Reactive Medium for Gold Nanoparticles and Nanocomposite Materials**

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The preparation of advanced materials using elemental sulfur is of increasing interest for emerging areas in materials chemistry and energy technologies. The current global production of elemental sulfur is on the order of 70 million tons annually, the majority of which is produced from refining of petroleum products through hydrodesulfurization.[1a] Traditional utilization of elemental sulfur is directed toward the production of commodity chemicals, such as sulfuric acid and phosphates as fertilizers for agrochemicals. Smaller niche markets for specialty chemicals, such as rubbers (e.g. tires) obtained by vulcanization processes also directly utilize elemental sulfur. Despite these existing technologies, nearly seven million tons of sulfur are produced in excess, the majority of which is stored in powder form, or as compressed bricks in exposed, above-ground megaton deposits (Figure 1).[1b] Hence, the sheer abundance of elemental sulfur offers opportunities to develop new chemistry and processing methods to utilize sulfur as a novel feedstock for synthetic advanced materials.

A number of technologies have been realized which consume elemental sulfur. Sulfur has been extensively used as a reagent in organic synthesis[1c] and in nanomaterials synthesis (e.g. semiconductor nanocrystals).[1d] The incorporation of sulfur moieties into polymers has also been conducted to prepare organic films of high refractive index for optoelectronic applications.[1e] A recent demonstration of novel sulfur utilization was demonstrated by Fréchet and co-workers as resists for scanning probe lithography.[1f] In all of these existing systems, sulfur was a minor constituent of the total composition of the material used for these various applications. A notable exception is in the area of energy storage, where elemental sulfur has been demonstrated to be a lightweight, cathode material of high energy density for lithium–sulfur batteries.[2] However, because of both the inherently poor electrical and mechanical properties of elemental sulfur, direct utilization of sulfur as material for these emerging applications remains challenging.

Figure 1. Example of megaton sulfur storage block nearly 18 m in height, courtesy of Alberta Sulfur Research Ltd.

Efforts to either modify or utilize elemental sulfur to create polymeric materials have been investigated by both polymerization and processing methods. It has long been known[3a,b] that under ambient conditions, elemental sulfur primarily exists in an eight-membered ring form (S_8) which melts at temperatures around 120–124 °C and undergoes an equilibrium ring-opening polymerization (ROP) of the S_8 monomer into a linear polysulfane with diradical chain ends, above 159 °C (i.e. the floor temperature). (Co)polymerization strategies with S_8 have been developed through anionic ROP,[4a] free-radical processes,[4b] step-growth copolymerization with cyclic disulfides,[4c,d] and precipitation approaches for core–shell colloids[4e,f] to modify the properties of sulfur. The preparation of nanocomposite materials with elemental sulfur is a new opportunity in materials chemistry that has not been extensively explored. Because of the incompatibility of sulfur with the majority of chemical reagents, composites with high sulfur content and colloidal inclusions have typically required high-energy milling.[2b] Multi-step synthetic approaches have more recently been

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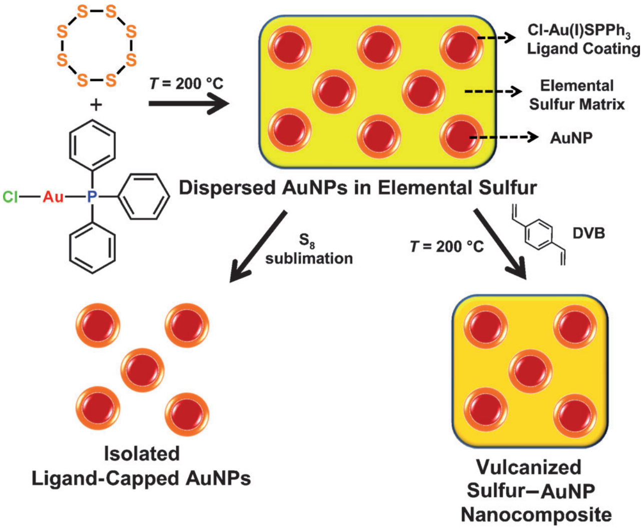
explored as demonstrated by Du et al., for the preparation of graphene oxide–sulfur nanocomposites, which enabled enhancement of the electrical conductivity.[4g] However, there are currently no reports on the direct modification of elemental sulfur with dispersed fillers, or nanoinclusions without the need for multi-step processing methods. Hence, there is a clear opportunity to develop new sulfur chemistry for these types of nanomaterials.

Herein, we report on the utilization of elemental sulfur as a novel medium for the formation of AuNPs and for in situ cross-linking of these colloidal dispersions to form vulcanized nanocomposites (Scheme 1). We report for the first time the direct dissolution of organometallic Au^I complexes in liquid sulfur for the formation of discrete, dispersed metallic AuNPs. Furthermore, to enhance the mechanical properties of these dispersions, reaction of the elemental sulfur matrix with divinylbenzene afforded cross-linked nanocomposites with AuNP inclusions. To the best of our knowledge this is the first example of direct utilization of elemental sulfur as a solvent and reactive medium for the preparation of nanomaterials, which is analogous to related reports using unconventional media, such as, ionic liquids, for the formation of nanomaterials.[5]



Scheme 1. Synthesis of AuNPs in elemental sulfur followed by either sublimation of free sulfur to afford isolated ligand-capped AuNPs or vulcanization of the sulfur–AuNP reaction mixture to form cross-linked nanocomposites.

The general strategy for the preparation of Au nanoparticles and nanocomposites was the direct dissolution of organometallic complexes and vinylic monomers into liquid sulfur without the need for additional organic solvents. Nonpolar complexes such as gold(I) triphenylphosphine chloride ($ClAu^IPPh_3$) and gold(I) chlorocarbonyl ($ClAu^ICO$) were found to be soluble in liquid sulfur at temperatures above 120 °C and were initially used for the synthesis of AuNPs.

For the preparation of AuNPs in liquid sulfur, elemental sulfur was heated in bulk to 200 °C, which resulted in the formation of polymeric sulfur as noted by the vitrification of the medium and a deep red color. The addition of $ClAu^IPPh_3$ (5 wt % relative to S_8) in powder form to this viscous mixture at 200 °C afforded a homogeneous brown solution, which within a few minutes exhibited a drastically reduced viscosity, relative to the polymeric sulfur mixture formed at this temperature. The physical appearance of this reaction mixture after the addition of $ClAu^IPPh_3$ at 200 °C was significantly different relative to pristine elemental sulfur (Figure 2c). Furthermore, isolated powders from this reaction could be re-melted at 140 °C to form stable, brown colloidal dispersions (Figure 2d). To increase the loading and yield of AuNPs within sulfur matrices, the pre-dissolution and concentration of $ClAu^IPPh_3$ (50 wt % relative to S_8) and elemental sulfur was conducted in carbon disulfide (CS_2) to form homogeneous composites, followed by heating to 200 °C. To enable the characterization of AuNPs, removal of free elemental sulfur was conducted by sublimation to afford brown powders which were sparingly dispersible in CS_2 (see the Supporting Information for the calculation of yields). We also note the evolution of a gaseous by-product from the reaction, which was found to be Cl_2 resulting from the reduction of the Au^I precursor to Au^0 NPs.

Transmission electron microscopy (TEM), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS) of isolated powders were conducted to confirm the formation of discrete, non-aggregated metallic AuNPs. TEM of AuNPs prepared using a loading of 5 wt % of the Au^I precursor

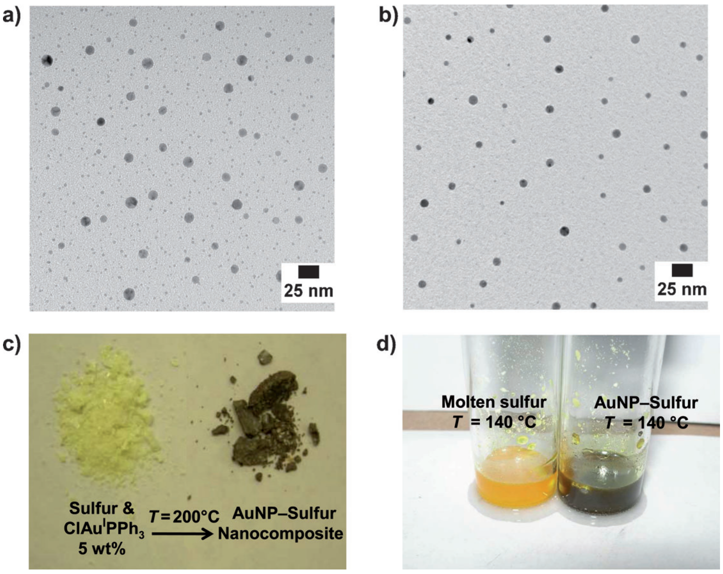
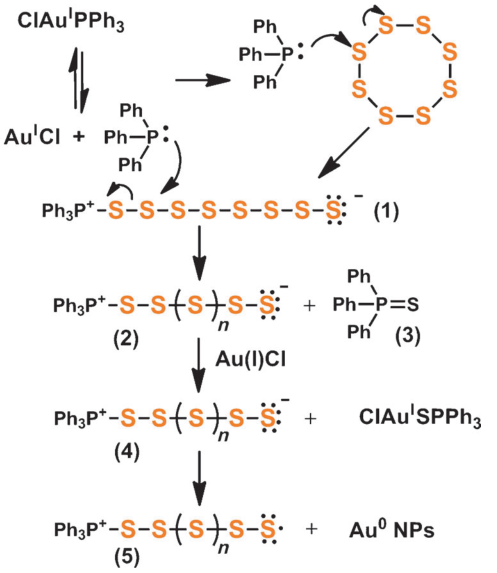


Figure 2. a) Transmission electron micrograph of AuNPs with diameters of 5.1 ± 3 nm formed directly in liquid sulfur using 5 wt % $ClAu^IPPh_3$. b) Transmission electron micrograph of AuNPs with diameters of 6.9 ± 2 nm formed using 50 wt % $ClAu^IPPh_3$ by predissolution with sulfur using CS_2 and removal of the solvent. c) Digital image of the sulfur–$ClAu^IPPh_3$ reaction mixture before (left) and after AuNP formation (right) at 200 °C and cooled to room temperature d) Neat liquid sulfur at 140 °C below floor temperature for the ring-opening polymerization (left) and the molten form of AuNP–sulfur nanocomposites formed at 200 °C, cooled to room temperature, and re-melted at 140 °C (right).

afforded colloids of spherical morphology with a broad distribution of the particle diameters ($D = 5.1 \pm 3$ nm) (Figure 2a). Similarly, AuNPs prepared with a 50 wt% loading of $ClAu^IPPh_3$ also exhibited a spherical morphology and slightly larger particle size ($D = 6.9 \pm 2$ nm) (Figure 2b). Powder XRD of isolated materials after sublimation confirmed the formation of metallic face-centered-cubic (fcc) gold of low crystallinity, as noted by broad diffraction peaks at 2θ of 38, 44, 64.5, and 77° (see Figure S5 in the Supporting Information). XPS of similar samples confirmed the formation of zero-valent gold by the photoemission of core electrons with binding energies of 82.7 and 86.3 eV, corresponding to Au $4f_{7/2}$ and Au $4f_{5/2}$ spin–orbit components (see Figure S7 in the Supporting Information).

An important finding in this system was the serendipitous role of triphenylphosphine (PPh_3) derived from $ClAu^IPPh_3$ to solubilize Au^I salts in liquid sulfur and form the ligand species required for AuNP formation. In the absence of PPh_3, Au^ICl was insoluble in liquid sulfur and gave large microsized Au agglomerates. In contrast, the external addition of one molar equivalent of PPh_3 along with Au^ICl and S_8 afforded a homogeneous solution when melted above 120 °C and formed discrete AuNPs ($D = 5.4 \pm 4$ nm) when further heated to 200 °C (see Figure S8 in the Supporting Information).

A second key finding was the recovery of chloro(triphenylphosphine sulfide) gold(I) ($ClAu^ISPPh_3$) crystals from dispersions of isolated AuNPs (i.e. after sublimation of sulfur) in CS_2 (see Figure S9 in the Supporting Information). It can be postulated that the formation of the triphenylphosphine sulfide ($SPPh_3$) ligand, which is necessary to form the $ClAu^ISPPh_3$ complex in situ, occurred through dissociation of PPh_3 from the $ClAu^IPPh_3$ precursor, followed by reaction with S_8. The mechanism is supported by the findings of Bartlett and Meguerian,[6a] who reported that PPh_3 readily attacked S_8 to afford a betaine intermediate (**1**, Scheme 2) with a positive charge on phosphorus and a negative charge on the displaced sulfur atom. Nucleophilic attack of an additional PPh_3 on intermediate **1** resulted in the formation of $SPPh_3$ and a shortened betaine (**2**, Scheme 2), where $SPPh_3$ re-complexes with Au^ICl in the sulfur phase to form $ClAu^ISPPh_3$. The $ClAu^ISPPh_3$ precursor is then likely reduced by anionic polysulfides, which are known reducing agents for Au^{III} salts to form zerovalent AuNPs (Scheme 2).[6b] Further evidence for this mechanism was confirmed by a final control experiment using Au^ICl, S_8, and externally added $SPPh_3$ at 200 °C. Under these conditions, discrete, non-aggregated AuNPs of size and morphology comparable to Au colloids ($D = 6.5 \pm 3$ nm) formed from the $ClAu^IPPh_3$ precursor, which confirmed the critical role of $SPPh_3$ as the key intermediate to solubilize Au^ICl in liquid sulfur and facilitate the formation of AuNPs (see Figure S10 in the Supporting Information). Given the findings of these different experimental conditions and other control experiments (see the Supporting Information), it is important to note the possibility of alternative reducing species and reaction pathways in addition to those from in situ generated polysulfides. However, in the presence of PPh_3, it is likely that the AuNP reaction proceeds through the proposed mechanism as described in Scheme 2.



Scheme 2. Proposed mechanism for the formation of AuNPs in liquid sulfur using $ClAu^IPPh_3$.

Further characterization through NMR, laser desorption/ionization mass spectrometry (LDI-MS) of isolated AuNPs after sublimation confirmed that $ClAu^ISPPh_3$ served as a steric ligand coating imparting colloidal stability (see Figure S13–15 in the Supporting Information). The interactions of the $ClAu^ISPPh_3$ with the nanoparticle surface are still under investigation, however, we hypothesize that Au^I–Au^0 interactions are present given the precedence for "aurophilic" bonding between Au^I complexes.[6c]

In addition to the formation of AuNPs in sulfur, vulcanization of crude Au–S reaction mixtures was conducted to improve upon the poor mechanical properties of these materials. In this system, the direct addition of divinylbenzene (DVB) at elevated temperatures ($T > 180$ °C) to reaction mixtures of sulfur and AuNPs was conducted at both low and high NP loadings (from 5 and 50 wt% $ClAu^IPPh_3$). Vulcanization with DVB of 4, 8, 16, and 33 wt% relative to sulfur–AuNP mixtures was performed, where nanocomposites with improved mechanical integrity were observed for formulations above 8 wt% of DVB cross-linker. Furthermore, DVB vulcanization of nanocomposites enabled microtoming of bulk samples mounted in cross-linked epoxy matrices for morphological interrogation by TEM (Figure 3a,b). In general, AuNPs of 7–9 nm diameters were found to be well-dispersed in vulcanized matrices of bulk nanocomposite samples at low filler loadings (Figure 3a). Aggregation of AuNPs into small flowerlike clusters was observed for samples with higher filler loadings. Interestingly, for samples prepared using 50 wt% $ClAu^IPPh_3$ and 16 wt% DVB, well-defined flowerlike clusters ($D = 24 \pm 5$ nm) were formed (Figure 3b), which most likely arose from depletion-induced aggregation of primary AuNPs as cross-linking of the matrix proceeded.

Raman spectroscopy of elemental sulfur and vulcanized nanocomposites confirmed the DVB–sulfur copolymerization as noted by the consumption of S–S vibrational stretches (153, 219, and 473 cm^{-1}) and the progressive increase of aromatic stretches (1442 and 1526 cm^{-1}; Figure 3c). After mechanical reinforcement of nanocomposites by vulcanization, free-standing Au–S films were fabricated by simple melt-press processing (Figure 3d). Melt-processing of AuNP–sulfur reaction mixtures without crosslinking only afforded liquids (when heated above the melting point of the matrix) which yielded granular solids with poor mechanical properties when cooled to room temperature.

In conclusion, we demonstrate the use of elemental sulfur as a solvent medium, reducing agent for Au^{I}, oxidizing agent for phosphorus(III), NP ligand, and cross-linking matrix for the synthesis of AuNP nanocomposites. This general approach is anticipated to open a new avenue of research for sulfur utilization by direct modification of elemental sulfur as a novel feedstock for material synthesis.

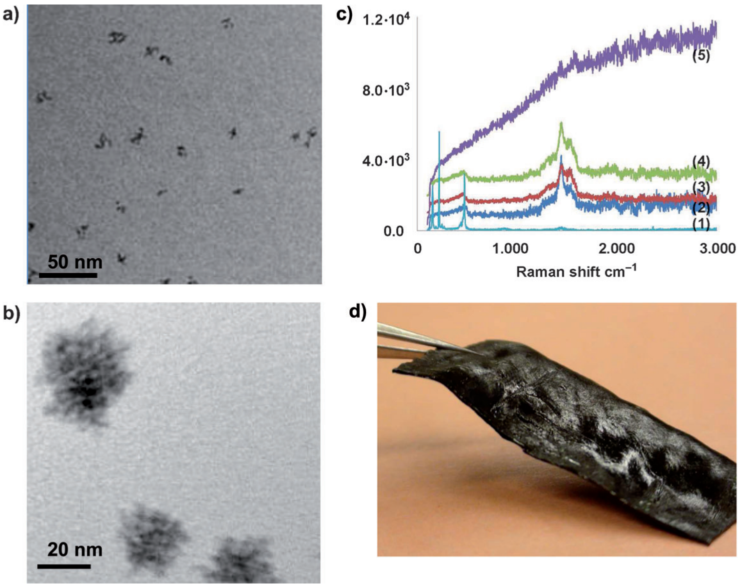


Figure 3. a) Transmission electron micrograph of microtomed films of cross-linked sulfur–AuNP nanocomposites prepared from 5 wt% and b) 50 wt% Au^{I} salts and after vulcanization with 32 wt% divinylbenzene. c) Raman spectroscopy of elemental sulfur (trace 1) and vulcanized nanocomposites with 4 (trace 2), 8 (trace 3), 16 (trace 4), and 33 wt% DVB (trace 5). d) Image of free-standing, melt-pressed films of cross-linked sulfur–AuNP nanocomposite prepared from 50 wt% Au^{I} salts after vulcanization with 33 wt% divinylbenzene.

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