

## Sonication-Assisted Synthesis of Large, High-Quality Mercury Thiolate Single Crystals Directly from Liquid Mercury

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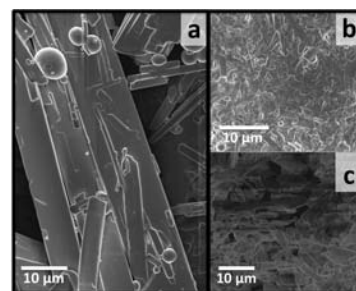
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**Abstract:** The synthetic formation of mercury thiolates has been known for almost 200 years. These compounds are usually formed by a slow reaction of mercury salts with thiolates or disulfides to produce small (up to 1  $\mu\text{m}$ ), plate-like crystals of  $\text{Hg}(\text{S-R})_2$ . Herein we show that such mercury thiolates can be formed directly from liquid mercury via sonication with neat thiols. The process not only produces crystals very rapidly (within seconds) but also leads to the formation of *large* crystals (up to hundreds of micrometers). The high quality of these crystals enabled their detailed structural characterization, which showed that the crystals are composed of ordered  $\text{Hg}(\text{thiol})_2$  stacks. We extended the experimental procedure to form and characterize a range of Hg thiolate crystals with various chain lengths. We propose a new self-assembly mechanism that can explain how sonication—which is usually used to break chemical bonds, to disperse materials, and to form nanosized crystallites—may lead to the growth of large, high-quality crystals.

The strong affinity of sulfur and more specifically of thiols for mercury, which results in the formation of mercury thiolate compounds, has received considerable interest over the years.<sup>1</sup> Potential applications of thiol-insulated Hg droplets in electronics has also recently attracted significant attention.<sup>2</sup> The synthetic formation of mercury thiolates has been known for almost 200 years. These compounds are usually formed by the reaction of mercury salts (nitrate, iodide, chloride, or cyanide) with thiolates or disulfides to produce  $\text{Hg}(\text{S-R})_2$ , followed by crystallization of the latter from ethanol.<sup>3</sup>

Since the first structural paper,<sup>3</sup> many researchers have been striving to solve and refine the structure of these crystals, but the generally small size of the crystallites rendered these attempts quite challenging.<sup>3,4</sup> It has been proposed that mercury thiolates demonstrate a crystal structure that exhibits planes of Hg ions separated by thiol bilayers.<sup>3,4</sup> Interestingly, in a 2D study, when the structure of alkanethiol self-assembled monolayers (SAMs) was investigated on the surface of liquid mercury, it was found that, with higher thiol coverage, multilayers perpendicular to the surface were formed with a repeating distance close to twice the alkanethiol length.<sup>5</sup> The authors postulated that this structure could be similar to that of mercury thiolate compounds synthesized from Hg salts but did not have sufficient data to confirm this hypothesis. Here we show a surprising result that large single crystals of Hg thiolate can be rapidly formed directly from liquid Hg by sonication with neat thiol.

Sonication can lead to cavitation, in which bubbles form and collapse, leading to a significant buildup of local pressures and temperatures for ultrashort lifespans.<sup>6,7</sup> Thus, this technique lends itself as a powerful synthetic tool that can be used to break chemical bonds and form nanosized crystalline materials.<sup>6</sup> It was therefore natural to expect that sonication of Hg in thiol would lead to the formation of nanometer-sized, thiol-stabilized Hg droplets. Surprisingly, however, when a mixture of liquid mercury (3 g, 0.015 mol) and an excess of neat 1-dodecanethiol (10 g, 0.05 mol) was subjected to a medium-intensity ultrasound, rapid phase transition was observed, resulting in the formation of large crystals instead of small droplets. This transition occurred after 5–10 s of sonication at 70% of the maximum power (200 W, 20 kHz S-250A Branson Sonifier), when the entire liquid abruptly emulsified, followed by the disappearance of the metallic silvery color of Hg and the formation of a silvery-black deposit. After the separation of small amounts of unreacted Hg droplets, this deposit revealed ribbon-like structures with a length of up to several hundred micrometers, a width of several tens of micrometers, and a thickness of about 100 nm (Figure 1a). The yield of ribbons was about 85%. It has been shown that sonication leads to either cavitation or very efficient mixing even without cavitation.<sup>8</sup> Moreover, it has also been demonstrated that sonochemical reactions could take place when no cavitation is present.<sup>8</sup> In order to test the importance of sonication in the observed process and to determine whether simple mixing would lead to the same results, liquid mercury and neat 1-dodecanethiol were thoroughly mixed with an upward flow stirrer at 750 rpm for over 3 h. No emulsification and ribbon formation was observed, suggesting that powerful sonication (and potentially the associated sonochemical effects) is required for the reaction to occur. The yield of ribbons decreases with reduced sonication energy and reaches ~5% at 10% power.



**Figure 1.** SEM images of mercury dodecylthiolate crystals grown by two different methods. (a) Crystals formed by sonication of liquid mercury in thiol after 5 s. (b,c) Crystals grown via mercury salt using the Wertheim<sup>9</sup> method: as synthesized (b) and after recrystallization for 3 days (c).

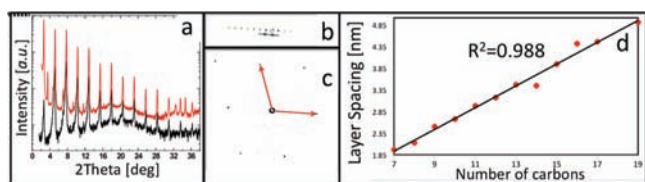
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Energy-dispersive spectroscopy (EDS) of the ribbons indicates that one Hg atom is attached to two dodecylthiolates. (Experimental values: C,  $88 \pm 1$  at. %; S,  $8.1 \pm 0.5$  at. %; Hg,  $3.9 \pm 0.3$  at. %. Theoretical values excluding hydrogen atoms: C, 89 at. %; S, 7.4 at. %; Hg, 3.7 at. %.) This ratio may suggest the formation of a Hg thiolate. To test this hypothesis, we grew dodecylthiolate crystals using the classic Wertheim method,<sup>9</sup> starting from Hg(CN)<sub>2</sub> and reacting with the alkanethiol in ethanol. This method led to the formation of submicrometer plate-like crystals (Figure 1b), which after slow, 3-day recrystallization from ethanol grew to several micrometers in size (Figure 1c) but were still significantly smaller than the deposits produced by the sonication method, which by contrast formed in several seconds.

Powder X-ray diffraction (PXRD) showed that the resulting crystalline structures are identical for the two methods of synthesis (Figure 2a), with a slightly stronger basal plane texture of the sample produced via sonication. Microbeam synchrotron XRD of individual platelets confirmed that each ribbon is a single crystal (Figure 2b,c). The spacing in the direction of the thickness of the ribbon was found to be 31.7 Å, which corresponds to roughly twice the length of the dodecanethiol molecule (15.2 Å). The spacings in the orthogonal directions within the layer are 3.7 and 4.1 Å. For comparison, the distance between Hg atoms in liquid mercury is 2.9 Å. These results show that sonication of liquid metal Hg in a neat thiol produces single crystals of mercury thiolate that are dramatically larger and better in quality than the crystals that can be formed by a conventional Hg salt-based synthesis.



**Figure 2.** XRD data for mercury thiolate crystals. (a) PXRD of mercury dodecylthiolate crystals grown from Hg salt (black) and liquid Hg by sonication (red). (b) Microbeam diffraction of a single crystal mercury dodecylthiolate (formed from liquid Hg). The layer spacing in the direction of the thickness (indicated by the two arrows) corresponds to 3.17 nm. (c) Diffraction pattern of the same crystal as shown in (b) but rotated by 90°. The indicated spots correspond to spacings of 3.7 and 4.1 Å. (d) Layer spacing in various mercury thiolates measured by PXRD as a function of the number of carbons in the alkanethiol backbone.

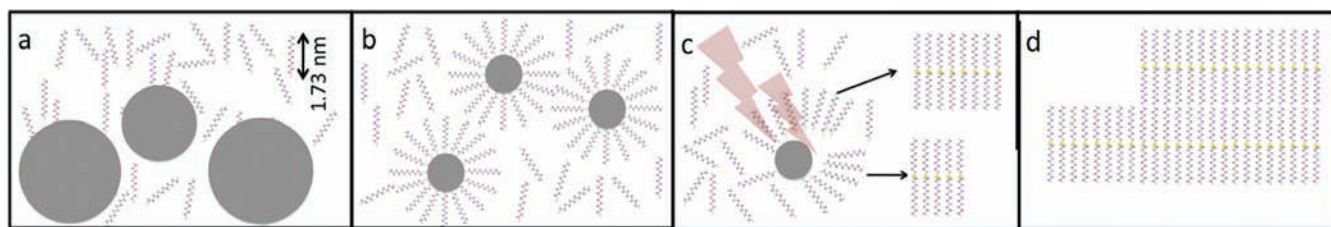
While the exact mechanism of the sonication-induced reaction is still unclear, we propose that the formation of the large single crystals of Hg thiolate may involve the following steps (Figure 3). At the first stage, the self-assembly of alkanethiol molecules on the surface of liquid mercury takes place (Figure 3a).<sup>5</sup> Sonication induces extensive breaking-up of the bulk Hg into small droplets, which immensely increases the surface area of the mercury in

contact with the alkanethiol. In the SEM image (Figure 1a), one can observe such small droplets that are stabilized by the thiol molecules, thus preventing their coalescence. The bonding energy of Hg–S (213 kJ/mol)<sup>10</sup> is ~12-fold higher than that of Hg–Hg  $17.2 \pm 2.1$  kJ/mol.<sup>11</sup> As the alkanethiols assemble on the surface of the mercury to form Hg–S bonds, additional alkanethiol molecules are competing with the neighboring mercury atoms. The huge difference in bonding strength between Hg–Hg and Hg–S is likely to promote the formation of S–Hg–S bonds near the surface of the liquid mercury and may lead to the generation of mono- and multilayers.<sup>5</sup> We envisage that sonication (with the associated cavitation or powerful mixing) facilitates this process and results in the detachment of entire SAM/Hg layers or multilayers from the surfaces of the Hg drops (Figure 3b,c).

The next step most likely involves the self-assembly of the mercury thiol layers in stacks, which nucleates the ribbon-like crystals (Figure 3c). The driving force for this step is similar to the formation of 2D crystals of alkanethiol SAMs on the surface of coinage metals and is governed by the van der Waals forces between long alkane backbones with bonding energy of about 1 kJ/mol per CH<sub>2</sub> group.<sup>12</sup> Due to the high energy input into the system occurring during sonication, such shedding of the preassembled layers of Hg(thiol)<sub>2</sub> continues until the entire liquid Hg is consumed. Since the crystal growth occurs through the addition of large, preassembled layers, this process is faster, and the resulting quality of the growing crystals composed of the stacked layers of Hg(thiol)<sub>2</sub> (Figure 3d) is significantly higher, compared to the thiolates formed using the Hg salts. The proposed mechanism involving the stacking of layers of mercury thiolates was confirmed by the observation that no crystals formed by sonication when alkanethiols with a chain length of fewer than four carbons were used, while crystallization occurred in the control experiments involving salts. This suggests that van der Waals forces between the alkane backbones would stabilize preassembled layers of Hg(thiol)<sub>2</sub> when the molecules are sufficiently long and, therefore, strongly supports the idea that a self-assembly mechanism is involved in the formation of large single crystals of Hg thiolate from liquid mercury.

Further investigations, performing the same synthetic procedure using alkanethiols with long alkyl chains (C<sub>n</sub>H<sub>2n+1</sub>SH,  $n = 7-17, 19$ ), demonstrate that the formation of large mercury thiolate crystals via sonication is a general reaction. The layer spacing measured by means of XRD correlates extremely well with the number of carbons in the alkanethiol backbone (Figure 2d), confirming that the crystals are composed of highly ordered, stacked Hg(thiol)<sub>2</sub> layers.

In conclusion, we have demonstrated a new powerful, rapid method to produce large, high-quality mercury thiolate single crystals starting from liquid metal via sonication in neat thiol. The crystals formed by this method grow much faster (within seconds



**Figure 3.** Schematic presentation of the mechanism of formation of mercury thiolate crystals from liquid mercury. (a) Formation of Hg droplets due to the sonication in liquid alkanethiols. (b) Formation of SAMs on the surface of each droplet. (c) Detachment of SAMs from Hg droplets and formation of free-standing ordered layers. (d) Stacking of the layers to form large single crystals. For simplicity, the Hg droplets and the alkanethiol molecules are drawn at a different scale.

as compared to days) and are 2 orders of magnitude larger than those formed via the conventional method that uses mercury salts. The quality of the sonication-produced crystals allowed their detailed structural characterization, showing that the crystals for a broad range of alkanethiols are composed of regular, stacked Hg(thiol)<sub>2</sub> layers.

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**Supporting Information Available:** Sample preparation and crystal characterization. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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