

# Supporting Information: Acoustic Cavitation Generates Molecular Mercury (II) Hydroxide, $\text{Hg}(\text{OH})_2$ , from Biphasic Water/Mercury Mixtures

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## Abstract

Emulsification of elemental mercury in aqueous solution in the form of grey particles occurs upon exposure to intense sound fields. We show the concomitant formation of molecular  $\text{Hg}(\text{OH})_2$  in the solution phase reaching a saturation limit of 0.24 mM at 25°C. The formation of  $\text{Hg}(\text{OH})_2$  is consistent with the 'hot spot' model which suggests the formation of OH. as a result of acoustic cavitation; such radicals are proposed to combine with Hg to form the  $\text{Hg}(\text{OH})_2$  species here characterised using voltammetry.

# Contents

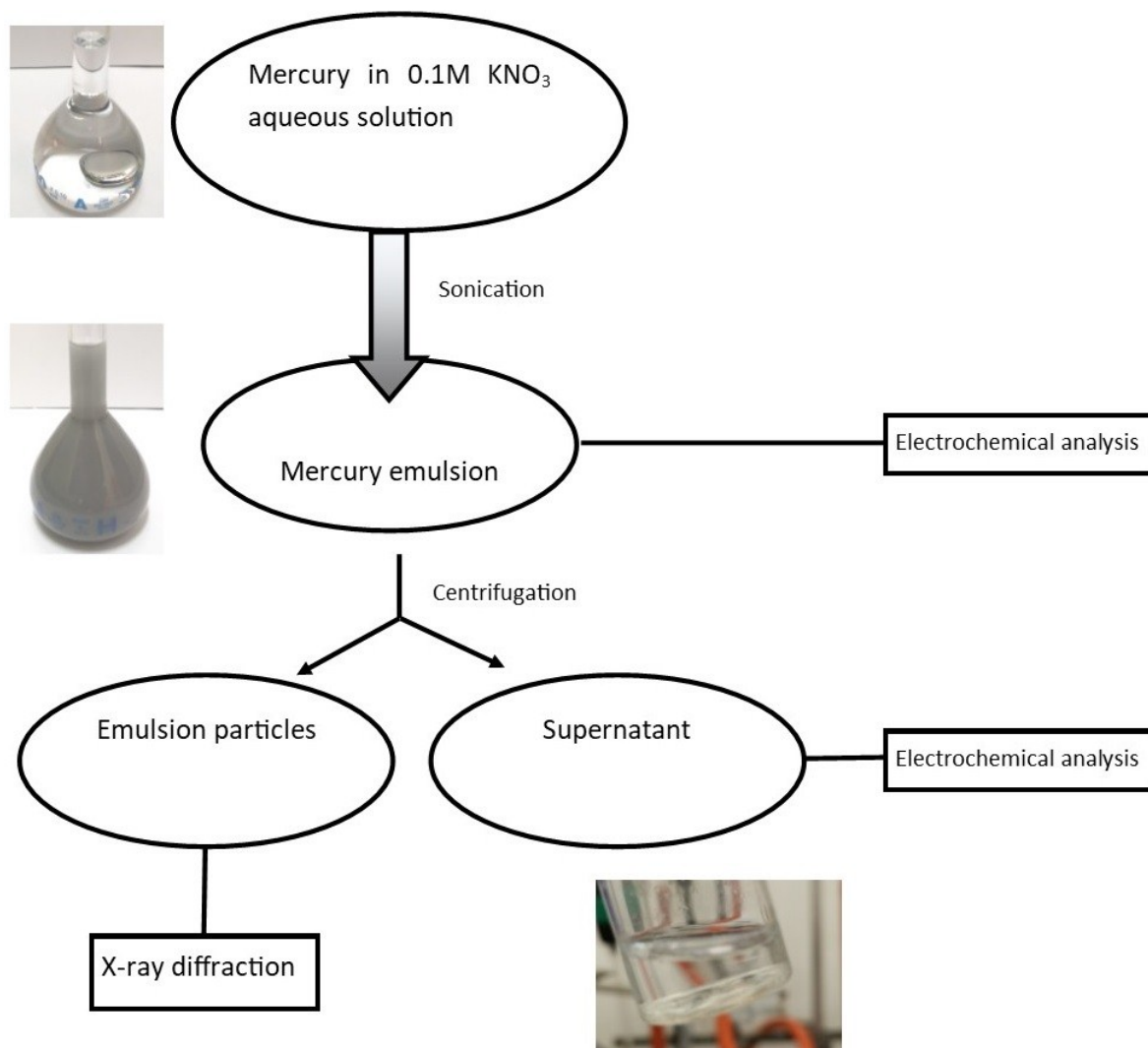
SI Section 1: Experimental Scheme

SI Section 2: Emulsion Particle Characterisation by X-ray Diffraction

SI Section 3: Spike Analysis

SI Section 4: Voltammogram of  $\text{Hg}(\text{OH})_2$  on a Platinum Electrode

## SI Section 1: Experimental Scheme



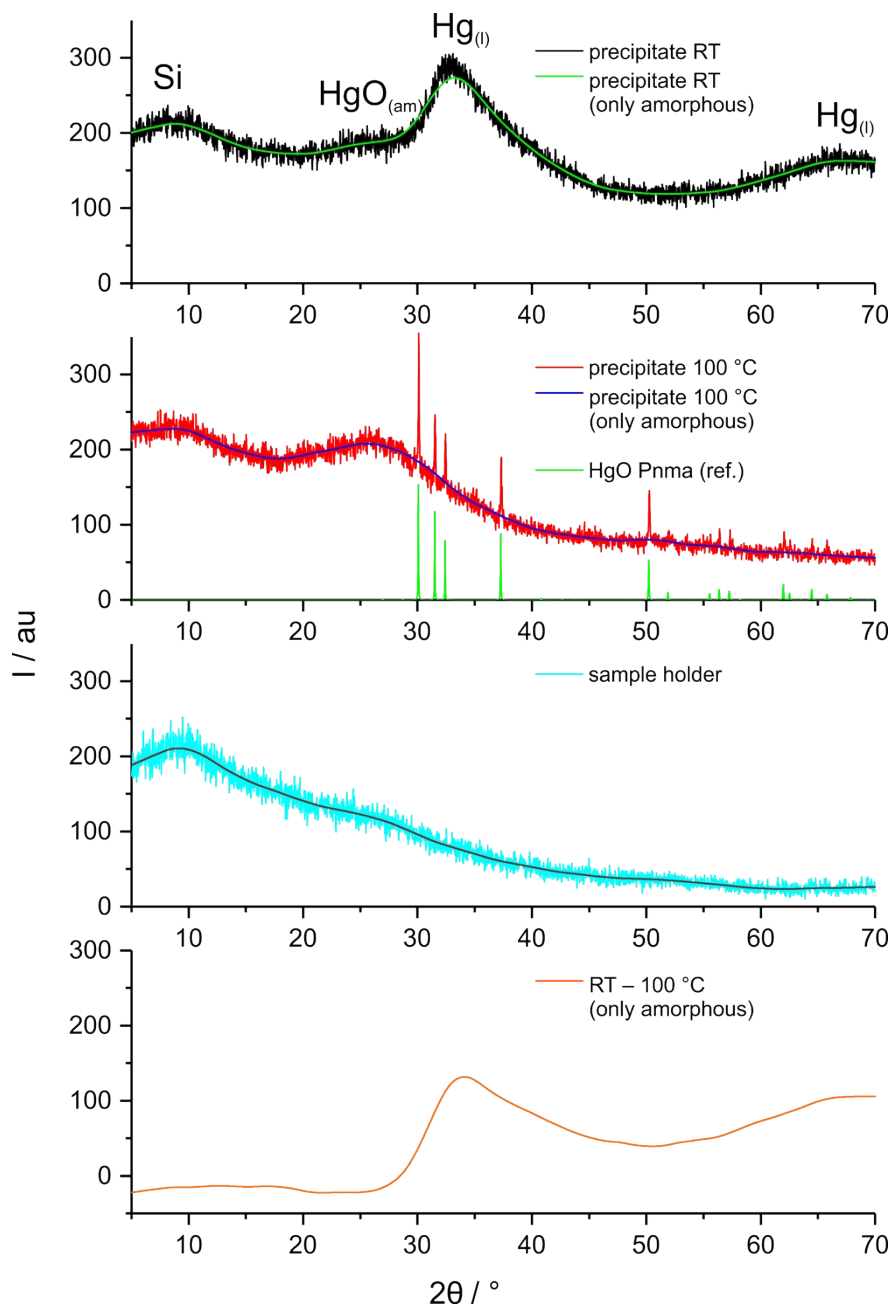
SI Scheme 1. Experimental scheme.

## SI Section 2: Emulsion Particle Characterisation by X-ray Diffraction Data

Insonation of the mercury/water biphasic system (see Experimental) led to emulsification of liquid mercury in water. The emulsion/dispersion particles were isolated via centrifugation and the X-ray diffraction patterns (XRD) measured, as shown in SI Figure 1.

At room temperature (RT), two broad peaks at approximately  $33^\circ$  and  $66^\circ$   $2\theta$  were seen and are consistent with liquid mercury,<sup>1-3</sup> while additional peaks at approximately  $9^\circ$  and  $25^\circ$   $2\theta$  can be observed. Upon heating in air to  $100^\circ\text{C}$  the peaks of the liquid mercury vanish and a sharp X-ray diffraction pattern emerges which corresponds to crystalline  $\text{HgO}_{(cr)}$  (*Pnma*, Pearson symbol oP8).<sup>4,5</sup> Nevertheless, the broad peaks around  $9^\circ$  and  $25^\circ$   $2\theta$  remain. The peak at  $9^\circ$   $2\theta$  is identified as amorphous scattering from the single crystal silicon sample holder (Figure 1, turquoise line). The peak at  $25^\circ$   $2\theta$  is related to the isolated particles and is essentially unchanged on heating; it is attributed to amorphous  $\text{HgO}_{(am)}$ . This can be seen by subtracting the  $100^\circ\text{C}$  data from the RT data (Figure 1, orange line), yielding the room temperature dataset with only the liquid mercury peaks.<sup>1-3</sup>

Therefore it is concluded that at room temperature the emulsion particles are composed of liquid Hg *and* amorphous  $\text{HgO}_{(am)}$ , with the latter most likely forming a thin shell around the liquid Hg resulting in the matt grey appearance and the prevented coalescence of Hg droplets. After heating to  $100^\circ\text{C}$  HgO exists in an amorphous and in a crystalline form. Note that Hg is lost on heating. To the best of our knowledge this is the first XRD study of an Hg emulsion and the first to show that it consists of Hg and amorphous  $\text{HgO}_{(am)}$ .

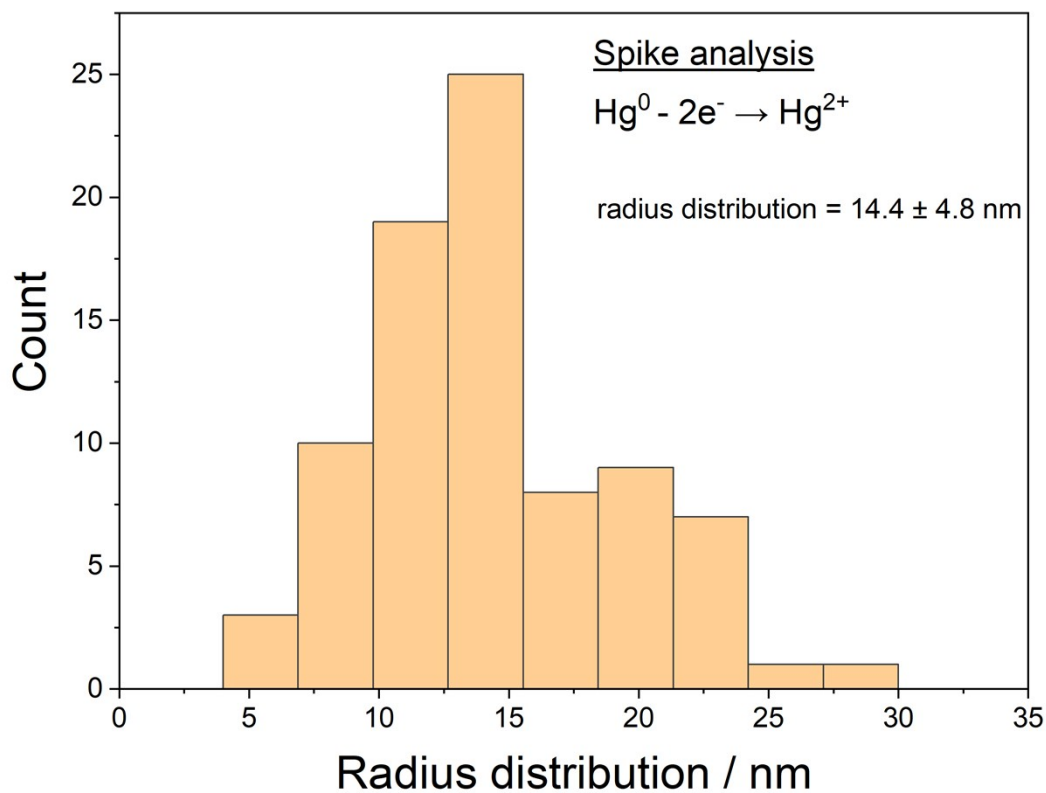


SI Figure 1. From top to bottom: X-ray diffraction data and the amorphous part of it (lowess filter) of the grey emulsion particles before (black, green), after (red, blue) heating to 100 °C in air, from the silicon sample holder (turquoise, brown) and the difference between after and before heating (orange; only amorphous part). For the heated sample crystalline  $\text{HgO}_{(cr)}$  (green; *Pnma*, Pearson Symbol *oP8*) is shown as reference.<sup>5</sup>

### SI Section 3: Spike Analysis

The oxidative spikes are only seen after the main oxidative stripping of bulk mercury and are ascribed to the incomplete oxidation of bulk mercury resulting in the loss of small mercury droplets either into the solution phase, and/or remnants on the electrode surface, leading to the sporadic oxidation spikes.

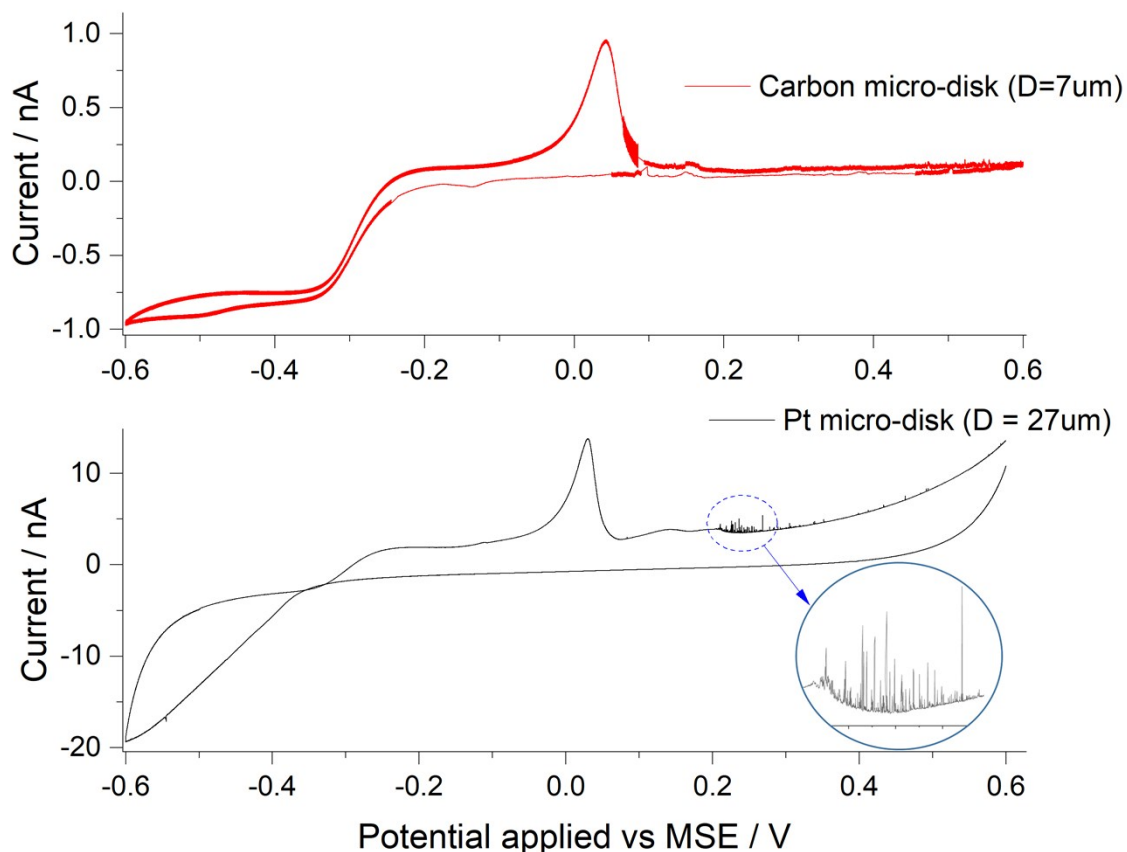
The spikes charge in the double-step chronoamperometry experiment (Figure 2, blue line) were analysed. The size distribution of the mercury droplets is shown in SI Figure2 with radius of  $14.4 \pm 4.8$  nm (calculated with number of electron transferred  $n = 2$  and assuming the droplets are spherical in geometry and are thought sufficiently small to undergo full oxidation).



SI Figure 2. Size distribution of mercury droplets analysed from the double-step chronoamperogram shown in Figure 2, blue line.

## SI Section 4: Voltammogram of $\text{Hg}(\text{OH})_2$ on a Platinum Electrode

SI Figure 3 shows a cyclic voltammogram of  $0.24\text{mM Hg}(\text{OH})_2$  recorded on a platinum (bottom, diameter =  $27\mu\text{m}$ ) and on a carbon electrode (top, diameter =  $7\mu\text{m}$ ; also shown in Fig 5, red line). Note the geometric area of the Pt micro-disc electrode is larger than the carbon electrode which result in larger recorded current. Apart from the broad and distorted reduction wave as seen on the Pt electrode, the potential at which the subsequent stripping of bulk mercury and the spiky peak occurs are similar.



SI Figure 3. CVs of  $0.24\text{mM Hg}(\text{OH})_2$  in  $0.1\text{M KNO}_3$  recorded at  $20\text{mVs}^{-1}$ ; top – Carbon micro-disk electrode (diameter =  $7\mu\text{m}$ , also shown in Figure 5, red line) and bottom – Pt micro-disk electrode (diameter =  $27\mu\text{m}$ )

## References

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