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A Smart Nanofibrous Material For Adsorbing And Real-Time Detecting Elemental Mercury In Air

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It is good to see research work attempting to develop new sensors for atmospheric mercury measurement. The scientific work done by the authors is worthy of publication, with major modifications, but more on that below.

The communication of scientific work should be held to a high standard, in my opinion. This English manuscript is very difficult to follow because of the poor grammar, sentence structure and basic mistakes; this impacts the scientific accomplishments. For example, the word *vapor* is replace by the word *fiber* throughout the document, including the references, suggesting it was translated by an automated program and never reviewed. I would estimate there are at least 100 places that need to be rewritten using acceptable English (missing words, misspelled words, confusing sentence structure and/or bad grammar). There are too many to correct. One example is line 333 "Sensing measurements, i.e. current (or resistance) changes, were provided in continuous." The poor English and mistakes should be fixed, or else the manuscript should not be published.

General comments on sensor technology

One of the justifications for developing the technology reported in this manuscript is the current system used in nearly all major national and international networks is complicated and costly, which limits the atmospheric ability to monitor mercury worldwide (line 86). I suggest that the limitation is the ultra-low levels of ambient mercury in the atmosphere. The typical background gaseous elemental mercury (GEM) level of 1.5 ng/m^3 is equivalent to 168 parts per quadrillion by volume (ppqv). There is no other atmospheric compound being measured routinely, continuously and automatically at this ultra-low concentration. Furthermore, current sensors in development, and even the equipment now used widely, are limited because of the need to collect mercury on a surface, like gold, with interferences commonly a million to billion times higher in concentration. Moreover, for routine long term monitoring the mercury collection surface and system must be able to perform with stability, precision, accuracy, frequent calibration and most of all robustness over long periods in a wide range of complex and changing environments (high altitude, urban sites, tropics, deserts and mobile research platforms). In research or commercial applications of automated, continuous air measurement technology, one near constant is that *complexity and cost increase as detection limit decrease*. The conductive sensor made with nanofiberous gold, describe in the manuscript was making measurements in the ppb range, at least 1 million times higher than what would be required to measure GEM in the background or urban air.

Specific critical comments to improve the manuscript

The use of "Smart" in the title seems to be over-reaching and may set expectations too high.

Based on the comments above, the abstract may also be suggesting way too much in the last sentence (line 25). At most it is a hope, or goal, that the sensor will be low-cost, very stable, low power and so on, since there was no scientific evidence or otherwise to give the reader the expectation that the claims will come true.

The justification and need for a new sensor was articulated very well. It may be useful to comment on the challenges and limitations every mercury scientists faces, due to the ultra-low part per quadrillion levels of mercury in the atmosphere.

Please define the basis for the units of ppt and ppb used in the manuscript. Typically concentrations for mercury used in the literature are mass/volume at standard temperature and pressure (e.g. ng/m^3). Most gas monitoring is reported in volume/volume (e.g. pptv). There is a factor of about 10x between ng/m^3 and pptv, which affects the understanding of the measurements made.

Since CH_3HgCH_3 was correctly listed as a gaseous oxidized form of mercury, then lines 44-45 must be changed, since dimethyl mercury is volatile and much less soluble that inorganic oxidized mercury forms.

The literature references of other mercury sensors using some form of nano-gold capture and detection was a good contribution to the manuscript. There was the suggestion that this sensor in comparison to other sensors has encouraging results (lines 319-310). It would have been useful to make a comparison of this work to the other mercury sensor technology being developed, for example Localized Surface Plasmon Resonance (LSPR) and state why this work is better or not. A table is recommended. Also, using a gold film and measuring the conductance change has been around for a long time as a successful, low-cost commercial instrument (Arizona Instruments, Jerome J405), able to measure Hg levels much lower than reported in this manuscript. How is the nanofiberous gold system an improvement over the Jerome J405?

The description of the nanofiberous manufacturing process appears to be rather complex. It is fairly well known that producing reproducible and robust surfaces with gold coating is difficult. While it was stated that the manufacturing process was reproducible (line 314), with references, there was no evidence provided that the reproducibility of the manufacturing, would in turn lead to a predictable response of the sensor, or when it may fail after repeated sample/heat cycles. It also appears that there were two different ways to make the nanofiberous material, with the second starting with electro-spinning and sol-gel techniques. Please clarify these two points with supporting evidence or at the minimum, comment on them.

The proof of concept, to measure low ppb levels of mercury in zero air, presented in the data figures and tables and discussed in the text is fairly well done. Some questions and comments do remain about the sensor such as:

- In Figure 7, when clean air is introduced, the current keeps changing, when it would seem that it should be constant with no new mercury being added. Please comment
- The need to have active flow over the sensor and use a curve fitting algorithm, begs the question of how the sensor system will be able to maintain accurate results when the Hg concentration varies over the 10 minute or longer sampling periods. For example, if the concentration was 20 ppb for 2 minutes and 8 ppb for 8 minutes, how would concentration be determined? I assume there would need to be some extrapolation between known response curves for different concentrations? Please comment.
- There was no evidence shown that the response curve is stable with time and repetitive heating cycles. Results of these experiments would be extremely valuable.
- Since there is active flow over the sensor, not through the sensor, there should only be a fraction of the gaseous mercury that is adsorbed onto the gold sensor surface (uptake rate).

Will the uptake rate change with flow rate, temperature of the sensor, and/or age of the sensor surface? Please comment?

- Since the goal and expectation, as written by the authors, is to measure true ambient level Hg concentrations of 200 ppqv or lower, please provide potential improvements and technical advances that would make this possible? As I understand it, the primary way to get to lower concentrations is very long sample times, which creates a number of trade-offs, such as no drift in electronics or temperature over time, greater potential for surface poisoning by interferences and most obviously, much lower resolution, to name just a few. It would be good to have the authors comment on the needed technical advances and their feasibility to reach the 200 ppqv level.

The conclusion seems good overall. In line 385, the phrase "highly sensitive to Hg^0" seems to be a bit of an overstatement and should be reworded. Further in line 385, there is a statement about being robust and resistant to solvents and VOCs in air, but there was no data to support it or that it will not behave just like any other gold surface used for mercury capture and detection. It would be better to state "that extensive experiments will be needed to determine if the gold surface will be robust against contaminants and interferences common in actual ambient air." In line 391, why is the nanofiberous gold not considered a "trap", since it must collect (trap) mercury over a known time and then is reheated to start a new cycle – I recommend this to be modified. The last line of the conclusion is the key point for future work and evaluation of the sensor, so it is good to see the recognition of the challenges ahead.