Reviewer 1
General comments.

The task of the atmospheric mercury monitoring network developing is very important for understanding the scale of emission, regional and global transfer, deposition of this environmental pollutant. Existing system of background monitoring is based on AFS and AAS instrumental observations requiring high investments for set up of any new monitoring point. That's why creation of new low-cost, hands off measurement systems is an imperative topical issue. The manuscript presents the results of the development of a novel sensor for air mercury measurements based on original manufacturing technology. The title reflects the contents of the paper, the mainresults are outlined in the Abstract. Introduction gives a comprehensive, 3.5 pages, review of the atmospheric mercury, speciation, mercury transfer, existing publications on the mercury sensors development. Principal part of the manuscript is devoted to description of a new sensor design and manufacturing technology, study of the absorptivity of the new material exposed to mercury vapour. Sensitivity of the new sensors is far not sufficient for the task of mercury monitoring declared in Introduction (see Specific comments, 1). No data on mercury measurement in ambient air, selectivity, and possible interferences are presented.

Specific comments
1) Commonly, in regulatory and scientific literature, the weight concentration units are used (ng/m3, pg/m3) for atmospheric mercury and mercury speciation. The authors use these units in Introduction, but different units: ppm, ppb, ppt in parts describing sensors. It is not explained what these units are related to: volume, mass, or number of molecules?

1) Authors agree to the Reviewer comments: scientists involved in monitoring mercury in atmosphere are used to adopt mass/volume as units. On the other hands, in scientific literature scientists involved in developing and characterizing the features of sensors or more complex devices are also used to employ units as ppm, ppb, ppt. In fact the scientific literature reported in this manuscript and related to sensors for mercury detection, reports mercury concentration in part per billion/trillion/million etc. Since the authors are describing the parameters of the proposed sensor as potential subject for atmospheric monitoring, units as parts per….were preferred.

We suppose the volume units are used. It is inconvenient, because a comparison with conventional concentration units requires recalculation
to the normal condition (P, T).

1a) Authors agree to the Reviewer about the necessity to clarify which kind of ppb (volume, mass, number of molecule). As described within the manuscript, a permeation tube was used as Hg generator and Tekran instrument as analyzer of the Hg^0 concentration. Thus a gas-tight syringe picked up defined microliters of air containing Hg° delivered in the measuring chamber and then injected into the analyser. When concentration was expected extremely high (800 ppb), the gas withdrawal was carried out upon a further dilution with the gas carrier. Tekran reported the results in ng/m^3, thus the final concentration was calculated taking into account the final volume (the dilutions) (5L/min - x5min) and then properly converted in ppm/ppb from the formula commonly used in environmental sampling and analysis ($C(ppb_v)$=concentration ($\mu g\ m^{-3}$) x V_{mol} (L/mol))/Molar Mass($gmol^{-1}$)). This is a conventional and common method to calculate the Hg concentration in laboratory, therefore was not described. Vice versa units as ppb will be marked with the subscript vol.

Besides, the “tiny” ppb values can create a false impression of enabling background Hg concentration measurements. For example, mercury concentration of 1 ng/m3 is about 0.1 ppt (vol). It turns the achieved “low”detection limit (LOD) and measurement range of “20 -100 ppb (LOD 1,5 ppb)” (see lines 23-24) to a quite high figures in conventional units: 200,000 – 1,000,000 ng/m3 (LOD = 15,000 ng/m3). For comparison, the concentration of saturated Hg vapour is 12,000,000 ng/m3 at 18 oC. Such sensitivity gives no possibility to monitor mercury in ambient air, as the LOD is 10,000 times larger than the average background mercury concentration of 1.5 ng/m3 (see line 75).

1b) Authors knew that the range in which measurements were carried out could be related only to very polluted scenarios: this concept has been reported within the manuscript and in the Conclusion paragraph. The concentration range was selected in order to describe some sensing performances such as the response time and its relationships with the concentration, and the calibration curve that allows to determine the range of concentration where the sensor responses have a linear curve shape (up to about 40 ppb). The limit of detection here reported has been measured taking into account the sensor response changes (shift of current after Hg exposure) after 10 min (response time was clearly reported). Thus it was the minimum value at which the analyte can be reliably detected in a 10 min-measure. It was calculated according to the literature as 3xStandard Deviation of the electrical signal (signal-to-noise ratio) multiplied by the response/concentration ratio (the slope of the response curve). In fact, in a previous work (Macagnano et al., submitted, Macagnano et al., 2015a) the authors reported a higher sensor sensitivity, with the possibility to detect up to dozens ppt, despite of a longer time necessary to reveal the analyte at these concentrations, in air. In this work the chance to apply the sensor in polluted sites and in real time has been presented and described (r145-149). Depending on the strategy of sampling and the coverage of the fibres, the limit of detection could be improved, about 2 ppt when slowly flowed within the measuring chamber (1 h measurement). However, despite the high sensitivity of the chemosensors to Hg0 vapour, the responses appeared to be slow.
What the present manuscript would like stress?
It describes the properties of a versatile sensor (ease of preparation, low cost apparatus) conductive at room temperature (low power) and sensitive to mercury vapours: this feature is depending on the time of exposure, due to the time necessary to entrap Hg enough to be detected as current variation. No carrier gas are required (it works in air). Sensor is robust: titania and gold are chemical compounds considered among the most robust materials. Thermal drift effects are expected to be lowered (only a 3min-heating process for desorption). Depending on the strategy of sampling and fibres treatments, the limit of detection could be improved. Potentials to be industrially fabricated (low cost of the process and the raw materials, electrospinning technology is commonly used in companies involved in textile, filtering and biomedicine) and used for large area monitoring (low dimension, low consumption, no gas carrier, no skilled operators). Their features make them promising candidates for sensor platforms (wired or WiFi connected).

2) How the LOD value was determined and at what exposure time? There is no description in the text. Different figures of LOD are presented in Abstract and Conclusion (compare lines 23-24 and 390-391).

2) Authors described the way they calculated LOD within previous answer

3) Lines 69- 70 “Since automated measurement methods of Hg require power, argon gas, and significant operator training, they are difficult to apply: : :” Argon is not required for AAS systems.

3) The Authors sentence collected the several drawbacks related to the conventional equipment for mercury detection. Obviously these instruments are extremely performing for mercury detection, and they generally need gold traps to work. The mercury analysers based on gold amalgamation and Atomic Absorption Spectrometry (AAS) detection are able to operate with ambient air as carrier gas. One or two pure gold traps are installed in series to run the dual amalgamation procedure and the sampling is run at about 1 L min-1 with sampling times of at least 10 minutes. Under these conditions, a detection limit of about 0.1 ng m-3 is achieved. On the other hand, some VOCs contained in ambient air may be adsorbed at the surface of the gold trap, and then can cause interferences (broad bands) to UV light spectral absorption of mercury at 253.7 nm.

4) Lines 105-107 “ decorated with gold nanoparticles (AuNPs) to obtain nanostructured materials capable of adsorbing GEM as a useful alternative system for making regional and global estimates of air Hg concentrations”. Gold adsorbs not only GEM.

4) The sensor is expected to be robust such as the commercial sensors based on metal-oxides are. The sensor is composed of TiO_2 and gold, two chemical compounds considered among the most robust materials since resistant to common solvents and VOCs as well as microorganisms attacks. Specifically titanium dioxide is insoluble in water, hydrochloric acid, dilute sulfuric acid, and organic solvents and almost insoluble in aqueous alkaline media. It could be dissolved slowly in hydrofluoric acid and hot concentrated sulfuric acid. Additionally gold is the most non-reactive of all metals, never reacts with oxygen (one of the most active elements) and water, which means it is not subjected to corrosion. Both the compounds are thermally stable also in extreme environmental condition. Additionally, the sensor is designed to work at room temperature (decreasing thermal drift effects are expected), being thermally treated only for a few minutes (up to desorb mercury from AuNPs (450°C). On the other hand, gold metal reacts with chlorine or bromine, iodine and it dissolves in *aqua regia* but doesn’t react with aqueous bases. Therefore, contaminated environments by halides and sulphides should affect the adsorption of mercury, thus cartridges or traps or coatings (as suggested in literature) for these interfering compounds should be used or gold nanoparticles should be properly functionalized (e.g. alkanethiols).

5) Lines 116-118 This is true that: “sampling rates (SRs) using the same passive samplers may depend on environmental conditions and atmospheric chemistry at each site. Moreover, it has been also highlighted that the performance of passive samplers may be influenced by meteorological factors (e.g., T _C, RH, wind speed) therefore inducing bias for the result of passive sampling (Plaisance et al.,. 2004; Sderstrm et al., 2004).” However, there is no evidence that the developed samplers are independent of meteorological factors (e.g. humidity) and interference of trace gases and aerosols, especially under long exposure time.

5) In a cocktail of other chemicals, this sensor has been designed as a pretty selective sensor, being able to greatly decrease the environmental disturbances allowing the investigator/manufacturer to design/fabricate easier strategies to prevent contaminations from environment (selective filtering systems or coatings). Among common potential contaminants authors investigated water vapour influence (%RH) reporting no-effects on the electrical signals **[Zampetti et al.,** Procedia Engineering 120 (2015) 422 – 426**]**, but obviously, experimental data concerning the effects of further interfering gas (as halides and sulphides), as well as other physical parameters will be subject of further investigation (as specified in Conclusions paragraph).

6) Lines 121-124 "In this work we describe an alternative approach adopted in the place of conventional ones demonstrating that the combination of gold affinity for Hg with a nanoscale sized framework of titania provided the chance to create promising sensors for environmental monitoring in real time, characterised by high sensitivity to the analyte." See note (1). Besides, the technology of real-time monitoring is not described.

6) Authors disagree with the Reviewer about this question since Figs. 7 and 10 are transient responses (i.e. real time electrical signal changes under defined mercury concentrations).

7) Lines 128-131. "The TGM/GEM sensor surface described here could be deployed in a global network such as GMOS; a permanent network of ground based monitoring sites and observations of Hg and/or related species on a global scale and with remote sensors would in fact be highly desirable". Again, see note (1). The achieved sensitivity is insufficient for background measurement at the level of few ng/m3 provided by GMOS stations, and for speciation study at the level of pg/m3. 8) Lines 333-338. For better understanding of sensing measurements: "The sensor was exposed to a flow of Hg0 336 in air with a concentration of 800 ppb for 1 min (Fig. 7, right)" In terms of standard units, we see that the sensor was exposed to almost saturated Hg vapour at 8 mg/m3. Thereby it is not clear how such high concentration was measured? Earlier (line 234), it was mentioned, that "The Hg0 concentration was checked by Tekran®2537A analyser". Tekran 2537 is not capable of measuring such high concentration.

7) About those questions, authors clarified in a previous comment the sampling methods.
Technical corrections
1) Numerous misprints: "fibers" instead of "vapour":
Lines 91-91: "cold-fiber atomic absorption spectroscopy : : :. cold-fiber atomic fluorescence spectroscopy"
Line 141: "Morphological, optical, electrical aspects and sensing measurements of fibers of GEM in air"
Line 144: "adsorbing and removal Hg fiber"
Thanks to Reviewer: all the typos and misprints have been properly modified
The same mistakes in the Reference list:
Lines 412-414 "Ferrua, N., Cerutti, S., Salonia, J. A., Olsina, R. A. and Martinez, L. D., 2007. On-line preconcentration and determination of mercury in biological and environmental samples by cold fiber-atomic absorption spectrometry. J. Hazard. Mater. 141 693–699" In the original Cold Vapour, see:
http://www.sciencedirect.com/science/journal/03043894/150
Lines 412-414 "Determination by Cold Fiber Atomic Absorption Spectroscopy. Analytical Letters 39" In the original Cold Vapour, see:
http://www.tandfonline.com/doi/full/10.1080/00032710600622167

2) Lines 73 -76 The sentence "Previous research highlighted that Hg-concentration levels in air vary greatly across different environmental locations, remote as the Polar Regions, background or rural, and urban locations with an average range between 1.5

ngm-3 (GEM) and 1 pgm-3 (GOM and PBM), depending on the speciation" should be revised: probably just by replacing "between" with "of".

A proper revision about typos has been provided.

Conclusion.
Obviously, an advanced comprehensive research has been done for the novel sensor design and manufacturing technology development. However, the sensitivity is far not sufficient to achieve the declared goal "to create promising sensors for environmental monitoring in real time, characterised by high sensitivity to the analyte" (lines 123-124). Probably, the new sensors can be used for other applications involving measurement of high mercury concentrations, such as technological or mercury exposure control.
I would suggest that the manuscript No acp-2016-1077, after suggested corrections, can be redirected for publication in a journal dedicated to sensor technologies, which will be more suitable for this kind of research than Special Issue "Global Mercury Observation System – Atmosphere" (GMOS-A). The proposed novel Hg sensor may be made more suitable for the use in the GMOS project upon its further development and improvement.

9) The authors conclusions are related to the resulting and then promising features of the sensor to be used for global mercury monitoring (low cost fabrication, low power consumption, no gas carriers, no skilled operators, miniaturization, versatility and potentials to be improved). Sensors provided with high surface area and porosity are suitable for exceptional interaction with environment, which means that, with the appropriate functionalisation, they are able to react with their target substance with great sensitivity. Therefore a potential commercialisation is significant. As previously explained, preliminary results are here reported: further investigation is required in order to design a final set-up configuration (an integrated microheater for desorption, a micropump, a set of filtering membranes for interfering) as well as an improved geometry of the sensor and the Hg delivery system. In Authors opinion and as reported within the manuscript, the proposed sensor sounds as one of the most promising sensors for mercury monitoring.

Reviewer 2

Peer Review of doi:10.5194/acp-2016-1077

A Smart Nanofibrous Material For Adsorbing And Real-Time Detecting Elemental Mercury In Air by Antonella Macagnano, Viviana Perri, Emiliano Zampetti, Andrea Bearzotti , Fabrizio De Cesare, Francesca Sprovieri and Nicola Pirrone

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.

Authors’ Answers

Authors thank the Reviewer 2 for his comments and suggestions in order to improve the manuscripts. About the English quality, authors agree to the Reviewer, then they proceeded to carefully review the manuscript’s language. That issue was partly caused by the kind of grammar language set on the several computers used to write manuscript: sometimes American and sometimes British English. The attempts to homogenize the languages failed by program errors and authors’ oversights.

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/m3 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.

Authors’ Answers

All the comments and suggestions of the Reviewer 2 have been taken in consideration and the manuscript has been revised accordingly (red types).

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.

1) 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/m3). Most gas monitoring is reported in volume/volume (e.g. pptv). There is a factor of about 10x between ng/m3 and pptv, which affects the understanding of the measurements made.

Authors' Answers

All the Reviewer 2 clarifications have been taken in consideration and the manuscript has been revised accordingly (red types).

2) Since CH3HgCH3 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.

Authors' Answers

The sentence has been properly modified.

3) 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 nanofibrous gold system an improvement over the Jerome J405?

Authors' Answers

A comparison with literature nanogold sensors has been added within the manuscript, as well as with the low cost commercial instrument of Arizona based on gold thin film (red types). The proposed sensor (LOD:2 ppt_v) was able to achieve comparable features of the Arizona system (Macagnano et al, 2017) under different measuring set-up systems. Long time measurements, reported also by Jerome J405, looked overcome by the flow rate. Furthermore the proposed sensor can be improved since subjected to further modification in density and size of AuNP, used with different or multiple transduction systems simultaneously (optical properties of nano-gold particles) and could be supported by spots of UV-light irradiation in order to enhance the titania contribution into Hg adsorption (the oxidized Hg).

4) 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 electrospinning and sol-gel techniques. Please clarify these two points with supporting evidence or at the minimum, comment on them.

Authors' Answers

The submitted paper of Ref. has been recently published (now is available on-line), thus the proposed manufacturing procedure and the results related to the fabrication and reproducibility can be visualized and used. Over the last 3 years of research, several sensors were used to measure the same concentration of Hg, and different sensors were investigated for different measurements, reporting comparable performances. About electrospinning and sol-gel techniques, there has been a misunderstanding: the electrospinning technique comprises sol-gel technique, when it is used to generate metal-oxide fibers, due to the precursor adopted for ES solution and calcination procedure. In order to avoid further misunderstandings, such a sentence has been clarified.

5) 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

Authors' Answers

Yes, that was probably due to the Hg still present in the line at the time of the Hg measurement stop. This effect has been confirmed by more recent measurements, where it disappeared when clean air never passed through part of tubes used too to deliver mercury to the measuring chamber.

6) 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.

Authors' Answers

The question is that changing the flow rate also the kinetics change. This effect and the strong relationships between the flow rate and sensor responses have been hugely investigated in literature. In the present manuscript only a specific flow rate (50 sccm) has been employed in order to understand if there was a relationship between the response curve and the concentration of the analyte selecting a few minutes of delivery time. Thus, using a selected flow rate you should have different transient response slopes for Hg^0 20 ppb and 8 ppb concentrations, respectively, regardless of final current shift after a 2-min or 8-min responses.

The major expectation is related to the chosen of the best flow rate, capable to improve response time and the LOD of the sensor.

7) 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.

Authors' Answers

At the state of art, authors measured the current values of the same sensor after several heating cycles in order to measure potential thermal degradation effects: no electrical degradation was reported after tens of measures. Under investigation are sensor morphology, drift and lifetime.

8) 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?

Authors' Answers

Yes, it would be. Sensor is exposed to a flow which impinges perpendicularly onto the surface of the sensor and then flows out from an exit positioned at the bottom of the sensor (outflow side). Temperature, age and flow rate are key parameters of the sensor.

9) 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.

Authors' Answers

Future expectations and strategies of improvements have been described within the manuscripts (red types)

10) The conclusion seems good overall. In line 385, the phrase “highly sensitive to Hg0” 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.”

Authors’ Answers

Line 385 has been reworded! About the sensor robustness and resistance, they are concepts coming from literature related to the physical, chemical and mechanical properties of gold and titania. Obviously extensive experiments will be needed to determine if the gold surface will be robust against contaminants and interferences common in actual ambient air. On the other hand, commercial systems (such as Arizona’s one) have been provided of scrubbers and filters to reduce the contamination of gold by other air pollutants .

11) 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.

Authors’ Answers

Line 391 has been clarified according to the Reviewer suggestion.

Revised Manuscript

Title

A SMART NANOFIBROUS MATERIAL FOR ADSORBING AND DETECTING ELEMENTAL MERCURY IN AIR

Authors

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Abstract

The combination of gold affinity for mercury with nanosized frameworks has allowed to design and fabricate novel kinds of sensors with promising sensing features for environmental applications. Specifically, conductive sensors based on composite nanofibrous electrospun layers of titania easily decorated with gold nanoparticles were developed to obtain nanostructured hybrid materials, capable of entrapping and revealing GEM traces from environment. The electrical properties of the resulting chemosensors were measured. Few minutes of air sampling were sufficient to detect the concentration of mercury in the air, in the range between 20-100 ppb, without using traps or gas carriers (LOD ~ 1.5 ppb). Longer measurements allowed the sensor to detect lower concentrations of GEM. The resulting chemosensors are expected to be low-cost, very stable (due to the peculiar structure), and requiring low power, low maintenance and simple equipment to work.

1 Introduction

Mercury (Hg) is released into the atmosphere both by human's activities, predominantly fossil fuel combustion, and naturally, for example, from soil out-gassing, volcanoes and evasion from the sea (Pirrone et al., 2010; Pacyna et al., 2010). One of the more troublesome questions in recent years has been to quantify not only the strength of emission sources but also the effects of re-emission of previously deposited Hg on the overall distribution, concentration and speciation of Hg in the atmosphere (Hedgecock et al., 2003). The deposition of atmospheric Hg depends on its chemical speciation, where the term speciation is used to distinguish between the gaseous elemental (GEM) and gaseous oxidized forms of Hg (GOM and Particle bound mercury-PBM) and their chemical-physical characteristics (Lyman et al., 2010; Sprovieri et al., 2016a,b). To be precise, total gaseous mercury (TGM) mainly comprises GEM with minor fractions of other volatile species (e.g., HgO, $HgCl_2$, $HgBr_2$, CH_3HgCl, or $(CH_3)_2Hg$). However, in spite of conceptual differences between TGM and GEM, they have often been used without clear distinction. This was allowable to a degree as the predominant fraction of TGM (usually in excess of 99%) is often represented by GEM under normal conditions. GEM is relatively inert under atmospheric conditions, only slightly soluble and also quite volatile, whereas several oxidized Hg forms found in the atmosphere are both soluble and involatile, thus they are efficiently scavenged and consequently deposited by liquid atmospheric water, such as rain and fog droplets, but also deliquesced aerosol particles. The dispersion of GEM on global scale therefore, depends on the rate of its oxidation in the atmosphere as this determines its long atmospheric lifetime (generally >1 year), limiting local emission controls from protecting all environments. Several international initiatives and programs (i.e., the United Nations Environment Program (UNEP)) have also made a tremendous effort in identifying and quantifying Hg pollution across the globe, especially the ‘‘hot-spots’’, aimed at reducing risk of exposure to this neurotoxin pollutant. Policy makers are working toward a worldwide effort for supporting the constructing an accurate global Hg budget and to model the benefits or consequences of changes in Hg emissions, for example, as proscribed by the Minamata Convention. Anticipating a global policy, in 2010 the European Commission began a five-year project called the Global Mercury Observation System (GMOS, www.gmos.eu) to create a coordinated global network to gaps in emissions monitoring and in the spatial coverage of environmental observations, mostly in the tropical regions and Southern Hemisphere, thus adequate for improving models and making policy recommendations (Sprovieri et al., 2016a,b). To date the GMOS network consists of more 43 monitoring stations worldwide distributed including high altitude and sea level monitoring sites, and located in climatically diverse regions, including polar areas (Sprovieri et al., 2016a,b). One of the major outcomes of GMOS has been an interoperable e-infrastructure developed following the Group on Earth Observations (GEO) data sharing and interoperability principles which allows us to provide support to UNEP for the implementation of the Minamata Convention (i.e., Article 22). GMOS activities are currently part of the GEO strategic plan (2016–2025) within the flagship on “tracking persistent pollutants”. The overall goal of this flagship is to support the development of GEOSS (Global Earth Observation System of Systems) by fostering research and technological development on new advanced sensors for in situ and satellite platforms, in order to lower the management costs of long-term monitoring programs and improve spatial coverage of observations. Since automated measurement methods of Hg often require power, carrier gases like argon, and significant operator training, they are difficult to apply for understanding Hg air concentrations and deposition across broad regional and global scales. Therefore, the lack of an inexpensive, stand-alone, low power, low-maintenance sensor is a primary technical issue to be solved for the sustainability of a global network such as GMOS. Previous research highlighted that Hg-concentration levels in air vary greatly across different environmental locations, remote as the Polar Regions, background or rural, and urban locations with an average range between 1.5 ngm^{-3} (GEM) and 1 pgm^{-3} (gaseous oxidized Mercury-GOM and particle bound mercury-PBM), depending on the speciation. Hence, for the determination of atmospheric Hg also at such low levels, sampling and analytical methods should be sensitive enough to quantify the concentration profiles of diverse Hg species in each respective environmental setting to better understand their environmental behavior and patterns. Fortunately, many advances made in analytical methodologies have made it possible to study atmospheric Hg in different environmental locations. However, several limitations and difficulties have still experienced in Hg analysis, as most methods cannot yet directly or accurately determine minor Hg species (Gustin et al., 2013). Hence, efforts should be continued to secure further the reliability, the traceability, and the accuracy of Hg levels measured in air. Current air monitoring devices are amply sensitive to detect the global background but are costly, complicated configuration, electricity requirements and high maintenance. A further limitation is the ultra-low levels of ambient mercury in the atmosphere. The typical background gaseous elemental mercury (GEM) level of 1.5 ng/m3 is equivalent to 168 parts per quadrillion by volume (ppq$_v$). There is no other atmospheric compound being measured routinely, continuously and automatically at this ultra-low concentration.

These features limit the scientific research community's ability to long-term measure atmospheric Hg concentrations worldwide. Sampling and analysis of atmospheric Hg is made most commonly as GEM/TGM because of their greater abundance, even if both manual and automatic methods have been currently developed for different Hg forms to suit the measurement and monitoring application. The most common sampling method employed relies on adsorption on gold amalgam and then, either directly or indirectly, through a stepwise process of thermal desorption and final detection [usually by cold-fiber atomic absorption spectroscopy (CVAAS) or cold-fiber atomic fluorescence spectroscopy (CVAFS)]. However, our knowledge presents currently several gaps to be solved. Firstly, the atmospheric chemistry of Hg remains poorly understood, especially the oxidation pathways by which GEM is converted to GOM, the reduction pathway which converts GOM back to GEM, and the gas-particle partitioning. This is partially due to the need for identification of the chemical forms of oxidized Hg in the atmosphere and methods to measure these compounds individually. In addition, the limitations and potential interferences with our current measurement methods have not been adequately investigated, thus alternate methods to measure atmospheric Hg are needed. Given the uncertainty and restrictions associated with automated and/or semi-automated Hg measurements (Gustin et al., 2013; Pirrone et al., 2013), and above all, responding to the technical needs of an expanding Hg global observation network, we developed a reliable, sensitive, and inexpensive surface for atmospheric Hg detection. In particular, we investigated and demonstrated the utility of composite nanofibrous electrospun layers of titania decorated with gold nanoparticles (AuNPs) to obtain nanostructured materials capable of adsorbing GEM as a useful alternative system for making regional and global estimates of air Hg concentrations. Methods and new sampling systems previously developed, such as passive samplers, have been used to understand long-term global distribution of persistent organic pollutants (POPs) (Harner et al., 2003; Pozo et al., 2004). Other passive samplers for both TGM and GOM collection on the basis of diffusion have been constructed using a variety of synthetic materials (i.e., gold and silver surfaces, and sulfate-impregnated carbon) and housings (Lyman et al., 2010; Gustin et a., 2011; Zhang et al., 2012; Huang et al., 2014). However, because of the differences in design of passive samplers, ambient air Hg concentrations quantified by various samplers may not be comparable. In addition, sampling rates (SRs) using the same passive samplers may depend on environmental conditions and atmospheric chemistry at each site. Moreover, it has been also highlighted that the performance of passive samplers may be influenced by meteorological factors (e.g., T °C, RH, wind speed) therefore inducing bias for the result of passive sampling (Plaisance et al., 2004; Sderstrm et al., 2004). On the other hand, incentive for developing simple and cost-effective samplers that are capable of monitoring over an extended period and require no technical expertise for deployment of these systems also at remote locations is now obvious. In this work we describe an alternative approach adopted in the place of conventional ones demonstrating that the combination of gold affinity for Hg with a nanoscale sized framework of titania provided the chance to create promising sensors for environmental monitoring in real time, characterised by high sensitivity to the analyte. The novel sensor is a relatively simple and low cost method for measurement of the most abundant Hg form in ambient air (TGM/GEM) due to reusable parts and simple deployment steps. Further, we have evaluated the applicability of this measurement technique with respect to real environmental conditions highlighting future directions of research on airborne Hg determination. The TGM/GEM sensor surface described here could be deployed in a global network such as GMOS; a permanent network of ground based monitoring sites and observations of Hg and/or related species on a global scale and with remote sensors would in fact be highly desirable. These data are needed to test and validate model processes and predictions, understand the source-receptor relationships, understand long-term changes in the global Hg cycle, and at least, would help policy makers to set regulations for different areas. The sensor features are related to the nanofibrous scaffold of titania capable of growing up gold nano-aggregates by photocatalysis, tunable in size and shape. Such a nanostructured layer, fabricated by electrospinning technology, firstly improves sensor features with respect to those of compact films, by enhancing the global number of binding sites of analyte-sensor and reducing some bulk drawbacks. Secondly, the combination of metal oxides and metal nanostructures, improves the sensitivity, allows sensor to work at room temperature, tunes selectivity towards different gas species by adjusting the surface to volume ratio of nanosized structures and affect sensor lifetime. Morphological, optical, electrical aspects and sensing measurements of fibers of GEM in air have been reported and discussed. When designed, the resulting Hg ad-absorbent material was expected to be suitable for novel Hg sensors fabrication, since a similar nanofibrous scaffold doped with AuNPs was described in literature as filtering systems capable of adsorbing and removal Hg vapor from the environment with an efficiency of about 100% (Y Yuan et al., 2012). In fact, in previous works **(**Macagnano et al., 2017 and 2015a**)** the authors reported a high sensitivity of the sensor, capable to detect up to dozens ppt_v, despite of a long time necessary to reveal the analyte at these concentrations, in air. In this work the chance to apply the sensor in polluted sites and in real time has been presented and described.

2 Materials and methods

2.1. Chemicals

All chemicals were purchased from Sigma-Aldrich and used without further purification: polyvinylpyrrolidone (PVP, Mn 1,300,000), titanium isopropoxide (TiiP, 99.999%), gold (III) chloride hydrate ($HAuCl_4$, 99.999%), anhydrous ethanol ($EtOH_a$) and glacial acetic acid ($AcAc_g$). Ultrapure water ($5.5 \cdot 10^{-8}$ Scm^{-1}) was produced by MilliQ-EMD Millipore.

2.2. Electrospinning technology

Electrospinning (ES) is a widely used technique for the electrostatic production of nanofibers, during which an electric field is used to make polymer fibers with diameters ranging from 2 nm to some micrometres from polymer solutions (or melts). It is currently the most economic, versatile, and efficient technology to fabricate highly porous membranes made of nano- and/or microfibers also for sensors (Macagnano et al., 2015b). It is based on the application of a high voltage difference between a spinneret ejecting a polymeric solution and a grounded collector. The jet of solution is accelerated and stretched by the external electric field while travelling towards the collector, leading to the creation of continuous solid fibers as the solvent evaporates. The electrospinning apparatus used in the present study (designed and assembled in CNR laboratories) comprised a home-made clean box equipped with temperature and humidity sensors, a syringe pump (KDS 200, KD Scientific) and a grounded rotating cylindrical collector (45 mm diameter), a high voltage oscillator (100 V) driving a high voltage (ranging from 1 to 50 kV) and a high power AC-DC (alternative current-direct current) converter. Electrospinning solution ($7.877 \cdot 10^{-5}$ M) was prepared by dissolving PVP in $EtOH_a$ and stirring (2 hours). A 2 ml aliquot of 1:4 (w/v) solution of TiiP solved in 1:1 (v/v) mixture of $AcAc_g$ and $EtOH_a$ was freshly prepared and added to 2.5 ml PVP solution under stirring in order to obtain a 1.95 (w/w) TiiP/PVP final ratio. Both mixtures were prepared in a glove box under low humidity rate (<7% RH). The syringe filled with the TiiP/PVP solution and housed in the syringe pump, was connected to a positive DC-voltage (6 kV), and set perpendicular to a 15 cm far grounded rotating collector. The substrates were fixed through suitable holders onto the collector (600 rpm, 21 °C and 35% RH) and processed (feed rate 150 ml h^{-1}) for 20 min to obtain scaffolds for sensors. After deposition, PVP/TiO_2 composite nanofibers were left for some hours at room temperature to undergo fully self-hydrolysis of TiiP (Li et al., 2003)and then annealed under oxygen atmosphere (muffle furnace) using a thermal ramp from room temperature up to 550 °C (1 °C min^{-1}, 4 h dwell time) in order to remove PVP and crystallize the metal oxide (*anatase*).

2.3 Transducers: interdigitated electrodes

The transducer adopted in the present work to convert the physico-chemical interactions of analytes with the different polymer fibers in an electrical signal was an interdigitated electrode (IDE) (Bakir et al, 1973; James et al., 2013). Specifically, the transducer, which consisted of 40 pairs of electrodes (150 nm in electrode thickness, 20 μm in gap and electrode width and 5620 μm in length),was manufactured in CNR laboratories through a standard photolithographic process (lift-off procedure), then followed by Ti sputtering and Pt evaporation, suitable to generate the electrodes of the size reported above, on a 4 in. oxidised silicon wafer. After electrospinning deposition all the electrical signals of the resulting chemoresistors were recorded by an electrometer (Keithley 6517 Electrometer).

2.4 Titania nanofibers

Upon calcination, the diameters of fibers extraordinarily shrunk: mean diameters of fibers were estimated through image analyses to be approximately within the range of 60–80 nm. Specifically, the resulting fibers appeared fine and rough at surface, with a fairly homogeneous fabric. The absence of beads and the good quality of the long and continuous fibers was confirmed through SEM micrographs. A highly porous and dense network of nanofibers covering the electrodes was observed, showing interconnected void volumes (porosity) and high surface-to-volume ratios (specific surface area). Zampetti et al., (2013) reported that such a fibrous layer showed a 99% of pores having an area less than 10 μm^2, with more than 80% pores being <1 mm^2.

2.5 AuNPs/TiO_2NFs photocatalytic decoration

Exploiting the photocatalytic properties of TiO_2, gold nanoparticles were selectively grown, under UV-light irradiation, on the electrospun titania nanofibers through the photoreduction of $HAuCl_4$ in the presence of an organic capping reagent (PVP). Thus the resulting fibrous scaffolds were dipped into an aqueous solution containing $HAuCl_4$ and PVP ($1.5 \cdot 10^{-3}$M and 0.1M respectively) and exposed to UV light irradiation for specified intervals (UV lamp 365 nm) (Helios, Italquartz). Depending on the gold nanoparticles sizes that were forming in photocatalysis, the dip-solution changed from light yellow to purple. Samples were rinsed extensively with water and then air-dried. Before morphological, electrical and sensing measurements, samples were heated at 450 °C per 1 h to eliminate the PVP traces. Morphological characterization were provided by scanning electron microscopy (SEM) (Jeol, JSM 5200, 20 keV) with pictures captured at 5 kV accelerating voltage. AFM (atomic force microscopy) micrographs were taken in tapping mode using 190Al-G tips, 190 kHz, 48N/m (Nanosurf FlexAFM). TEM (C-TEM, control transmission electron microscopy) micrographs were performed at 200 keV with an analytical double tilt probe. TEM specimen were prepared by gently scraping at first the TiO_2 nanofibrous layer electrospun onto the silicon support and then collecting the nanofibers, through adhesion upon contact with holy carbon thin film. UV-Vis spectra were provided by Spectrophotometer UV-2600 (Shimadzu), analyzing quartz slices coated with nanofibers. These substrates were able to collect fibers by electrospinning (20 min), and then were subjected to calcination according to the described above procedure, and then UV irradiation in the aqueous solution. The fibrous layer stayed stuck to the substrate if the thickness was thin enough. Longer depositions caused curling of fibers during the calcination process.

2.5 Measurement set-up

The sensor was placed in a suitable PTFE-made measurement chamber (0.7 ml volume) connected to an electrometer (Keithley 6517 Electrometer) capable of both measuring the current flowing through the IDE, when a fixed potential was applied to it, and sending data to a PC. Dynamic measurements were carried out at room temperature both using: (i) 4 channel MKS 247 managing four MKS mass flow controllers (MFC), set in the range 0–200 sccm and (ii) Environics S4000 (Environics, Inc.) flow controller, comprising three MFCs supplying different flow rates (up to 500, 250 and 25 sccm, respectively), managed by its own software. Pure air (5.0) (Praxair–Rivoira, Italy) was used as gas carrier. A homemade PTFE (polytetrafluoroethylene) permeation tube filled with a suitable amount of Hg^0 was included within such a delivery system to get set dilutions of Hg-saturated vapours. The tube was immersed in a thermostatically controlled bath, thus the desired Hg^0 concentration delivered to the sensor was achieved by both tuning the temperature of the permeation tube and the dilution flow. The Hg^0 concentration was checked by Tekran®2537A analyzer. Responses were calculated as $\Delta I/I_0$, where ΔI was the current variation and I_0 was the current when synthetic pure dry air was flowed. Sensor was restored after a quick thermal shot at 450°C under flow of pure air.

3 Results and Discussion

Nonwoven mats made of PVP and amorphous TiO_2 were obtained by the combination of electrospinning and sol-gel techniques (Fig. 1). The ES deposition was proceeding for 20 min on oxidized silicon wafers and IDEs, properly fixed on the surface of a conducting and rotating collector to form nanofibrous layers characterized by high surface areas and relatively small pore sizes (Zampetti et al., 2013). By changing the deposition time, both thickness and consistence of the mats changed. More specifically a 1h-deposition provided the formation of a thicker white and soft fabric, hygroscopic, soluble in both water and polar solvents and easily peeled off (Fig.1); instead a 20 min-deposition generated a fibrous film adhering to substrates, too thin to be weeded, thus preferred for sensors fabrication. The calcination process caused a complete degradation of PVP with formation of crystalline TiO_2 (*anatase*) and a significant shrinkage of fibers dimension (60-80 nm diameter, 5-40 nm grain sixe). Exploiting the photocatalytic properties of titania (*anatase*), a tunable decoration of fibers with gold nanoparticle could be achieved by dipping the fibrous mats in a proper aqueous solution ($HAuCl_4$, PVP) under UV light irradiation (Li et al, 2004; Macagnano et al., 2015). The photocatalytic reaction was proved by the color change of the solution (red purple from light yellow) (Fig.1). Changing both UV irradiation exposure time and PVP concentration, as capping reagent, morphology, size and density of gold nanoparticles could be tuned (Macagnano et al., 2017).

Figure 1. Sketch of an electrospinning set-up comprising a syringe and a grounded rotating cylinder collector where the samples take place for their coverage (*left*); a piece of a nanofibrous fabric of TiiP/PVP removed from the substrate after 1 hof electrospinning deposition (*centre*); a red-purple aqueous solution of $HAuCl_4$/PVP after UV-light irradiation treatment holding a piece of the nanofibrous fabric of TiO_2 (*anatase*) obtained after TiiP/PVP annealing (*right*)

In the present work, among a series of differently coated fibrous layers, only the fibrous nanocomposites that were conductive at room temperature were selected and then their electrical and sensing features investigated. The controlled gold deposition was due to the photo-excited electrons on the surface of TiO_2 nanofibers that were able to reduce the gold ions thus inducing gold metal deposition (Fig. 2, *the sketch*). The capping reagent was responsible of the shape of the particles. The surfaces of nanofibers, as observed in SEM micrographs (Fig.2, *right*), appeared densely decorated with globular nanoparticles. In C-TEM image (Fig.2, *inset*) the gold nanoparticles appeared darker with spherical or quasi-spherical shapes. The single particles sizes were ranging between 2 and 20 nm, with a 7.8±3 nm average diameter [(Macagnano et al., 2017). Gold nanoparticles grew directly onto the nanofibers and their adhesion appeared relatively strong (despite due to van der Waals forces), since they both resisted to water rinsing and fibers scratching for TEM analyses.

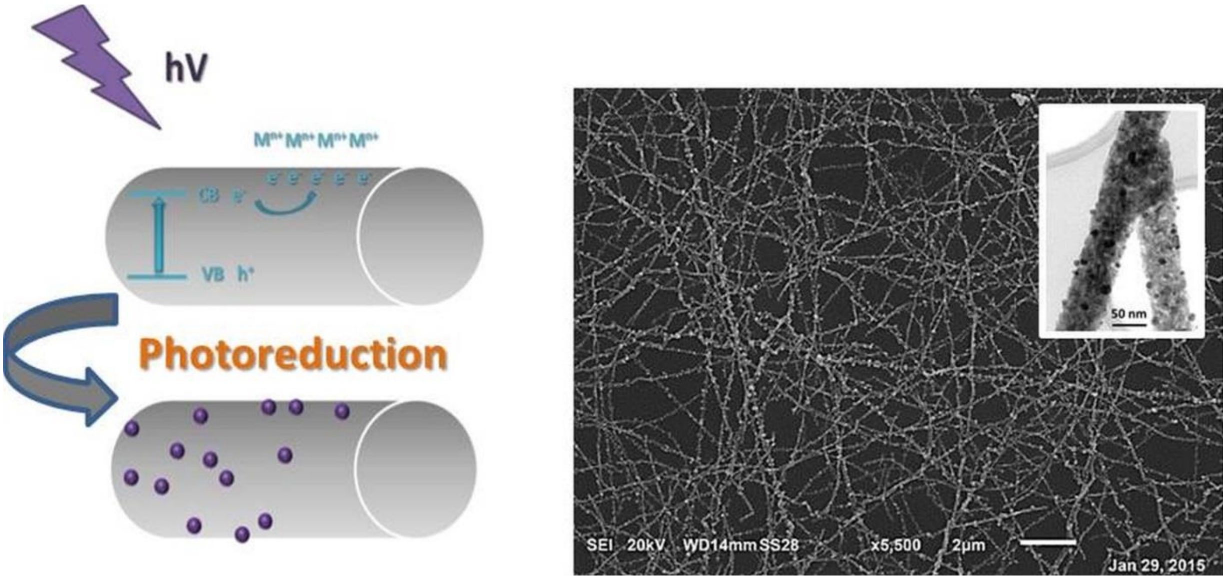

Figure 2. A sketch of the photocatalytic process occurring on the fibers surface (*left*); SEM picture of a dense nanofibrous network of AuNPs/TiO_2 coating a silicon wafer (*right*); a C-TEM micrograph of fibers finely decorated with gold nanoparticles (*the darkest ones*) bound without using any additional linker (*inset*).

As a result of the photocatalytic process, the white porous mat became purple-violet. As reported in the spectrum of the AuNP/TiO_2 hybrid system, a characteristic absorbance band appeared at about 543 nm, which corresponded to the surface plasmon resonance (SPR) of the AuNPs (Sun et al, 2003). A red shifting and broadening of the absorbance band was observed with the increasing in AuNP size and fiber loading, respectively (data not shown). The colour is strictly depending on the size of the nanoparticles, and then their agglomeration at the solid state. According to Bui et al. (2007), such a band broadening phenomenon is due to the electric dipole–dipole interactions and coupling occurring between the plasmons of neighbouring particles, whereas nanoparticle agglomeration phenomena occurred.

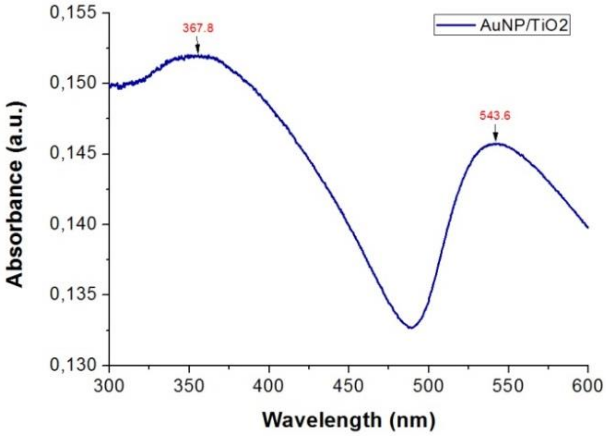

Figure 3. UV-Vis spectrum of a titania nanofibrous network after gold decoration (TiO_2: 367.8 nm; Au NPs: 543.6 nm)

Due to these features, UV-Vis absorption spectroscopy has been used in literature as a technique to reveal the changes in size, shape and aggregation of metal nanoparticles in liquid suspension after exposure to heavy metals, as Hg^0 (Morris et al., 2002). Both blue-shifted wavelength and its extent were proportional to the amount of Hg^0 that entered the liquid suspension. Similarly, when the gold decorated nanofibers of titania, collected on a quartz slice, were exposed to Hg^0 vapours (2 ppm) in air for 15 min, a significant blue shifting was reported (~ 3 nm) (Fig. 4) due to the atomic adsorption of GEM on the surface. The nanoparticles could be regenerated by heating the sample at 550°C for 3 min, thus removing all the Hg^0 adsorbed. Their recovery was stated by the achieving of the original values of wavelength (UV-Vis spectra). The regeneration process could be carried out for dozen times without any noticeable NPs deterioration. Similarly, the TiO_2 nanofibrous layers coating the metal electrodes of the transducers (Fig. 5), changed their colour after photocatalytic treatment (from white to pink).

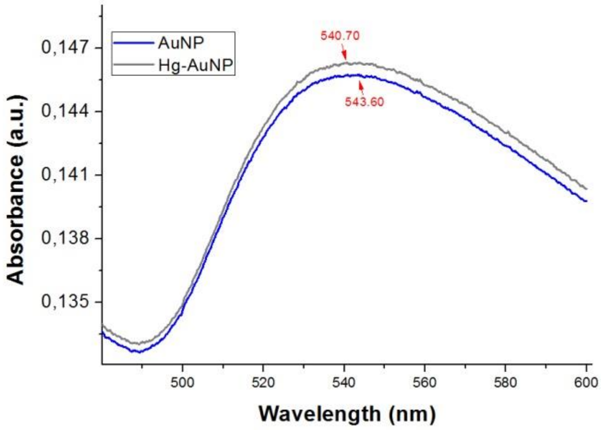

Figure 4. UV-Vis spectra of AuNPs/TiO_2nanofibers before (*blue*) and after a 15 min exposure to 2 ppm of Hg^0 (*gray*)

The IDE layout (Fig.5) comprises a set of interdigitated electrodes which occupies an area approximately 3x5 mm, completely coated with the sensitive fibers, and two bonding pads (2x2 mm) that will be connected to the electrometer (DC voltage). Such a planar interdigitated electrode configuration is the most commonly used for conductometric sensing applications.

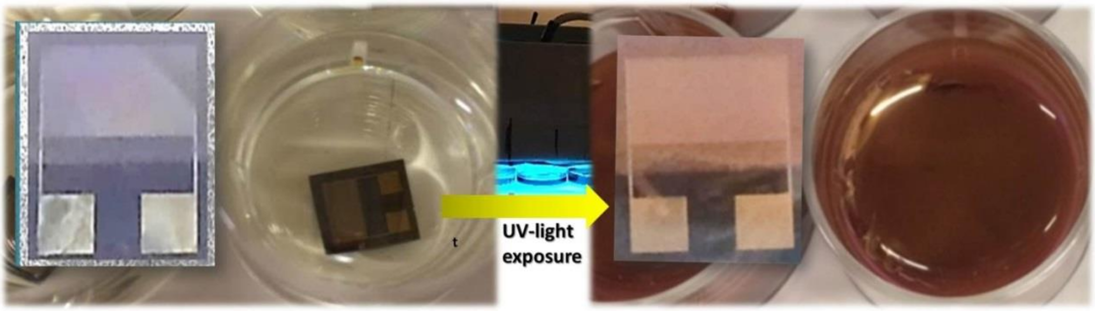

Figure 5. Chemosensor fabrication and final structure: IDE dipped (*left*) and exposed to UV-light (*right*) for gold decoration

Figure 6 depicts a Current–Voltage (I-V) curve of a chemosensor, under synthetic dry air flow. However curve shape was unaltered when air or nitrogen were flushed over the fibers (Macagnano et al., 2015), suggesting that oxygen concentrations poorly affected the electrical properties of such a chemoresistor. The resistance value of IDE coated with TiO_2 nanofibers before photocatalysis, resulted to be too high at room temperature to contribute straight to the final current value. The resulting linear shape (Ohmic behaviour) within the selected voltage range (from −3V to +3V) showed a constant resistance value for the sensor. The very low value of resistance (~1.2 k□) provided the chance to work at low voltage, with consequent effects on the energy consumption as well as lifetime of the material. Moreover, the linearity of I–V curve let us suppose that the sensing scaffold had a good adhesion to the metal electrodes. The electron conductivity has been supposed occurring according to the percolation model (Macagnano et al, 2017; Muller et al., 2003), since the titania at room temperature was expected to be an insulating matrix. When it is metal doped, the electron conductivity is ruled by thermally activated electron tunnelling from one metal island (gold nanoparticles) to the other. However, the conductivity of the nanocomposite is lower than that of pure metal (gold) because the electron mean free path is greatly reduced due to the presence of the dielectric (the titania crystals). The electrical features, such as the reproducibility of the fabrication process, of this conductive device have been previously investigated by the authors (Macagnano et al., 2017; 2015a), showing encouraging results for the development of a low cost sensor for mercury detection. However, in spite of the high sensitivity (LOD: 2ppt) of the sensor, too long response time was necessary to detect traces of Hg^0, overall if compared to the monitoring instrumentations (Ghaedi et al., 2006; Sanchez-Rodas et al., 2010; Ferrua et al., 2007) commonly involved in GEM detection. The long time in response was supposed to be in part due to the layout of the measuring system, since previously the sensor was housed in a quartz bottle of 100 ml volume. In fact an additional time is caused by the adsorption of Hg^0 traces from the surrounding environment (measuring chamber) up to achieve a sufficient number of Hg^0 atoms adsorbed on the surface sensor up to be electrically revealed. However, this sensor looks extremely encouraging if compared to other sensors currently involved in detecting mercury in air (Drelich et al., 2008; Kabir et al., 2015; Sabri et al., 2009; Mohibul Kabir et al., 2015; Raffa et al., 2006; James et al., 2012-2013; Chemnasiri et al., 2012; Sabri et al., 2011; Keebaugh et al., 2007; Crosby, 2013; McNicholas et al., 2011).

Many sensors have been designed and investigated to detect the several forms of mercury. Most of them have exploited the strong affinity between mercury and gold (Ford and Pritchard, 1971; Joyner and Roberts, 1973). Several studies have documented changes in the electrical properties, work function, and resistance of thin gold films upon exposure to various concentration of mercury vapor. For instance, an array of microcantilevers with different size, developed by Drelich et al., (2008), could measure different ranges of mercury concentration (between 37 and 700 µg/m^3), and were capable of revealing up to 10 pg Hg^0 adsorbed. However, their sensing system required both a dust-free gas carrier and a heating procedure (350 °C for 20 min) to regenerate the sensors. Gold-based conductometric sensors, too, have been designed and used to reveal mercury vapor through their electrical resistance changes (Raffa et al., 2006), but their sensitivity seemed often poor (about 1 µg/m^3). Quartz crystal microbalances (QCMs) devices, too, have been used as Hg^0 vapor sensors (Sabri et al., 2009) due to their high portability and selectivity, and no need for sample pre-treatments. Their absorptive capacity resulted improved (700 ng cm^{-2}) when the gold electrodes were made rough (more binding sites). However, additionally to the natural affinity of gold for mercury, the increased facility for producing and depositing nanoparticles with noble metals facilitated their use as possible sensors, overall in aqueous environments (Nolan and Lippard, 2008; Chemnasiri and Hernandez, 2012; Ratner and Mandler, 2015; Dong et al., 2015). James et al. (2012) developed a high sensitive chip working in a LSPR mode, based on gold nanoparticles (5 nm diameter) to monitor Hg^0 vapors. Such a system was able to linearly detect mercury concentrations from 1 to 825 µg/m^3, but it was strictly related to the flow rate: increasing the flow velocity (and mass transfer rate) increased the peak shift rate. The time resolution was limited by the rate of adsorption, which increased with Reynolds number: at the greatest flow rate tested (57 LPM), an ambient mercury measurement (1 ng/m^3) needed 410 h to shift 1 nm, but accelerating the flow rate the time resolution could be reduced.

Gold thin film technology has been recently adopted in a commercial portable device to detect mercury (Jerome® J405 Mercury Vapor Analyzer), with a 0.01μg/m^3 resolution and a 750 ± 50 cc/min flow rate (www.azi.com). A series of scrubbers and filtering systems are able to reduce the effects of interferents to the gold-mercury interaction. The flow rate and the measuring system layout resulted as key parameters into the proper working of the device. These features seem to be significant also for the ES-based chemosensor.

The measuring chamber was designed in order to reduce the volume (0.7 ml) and to expose the fibers to the gas entry (Fig. 7). Such a measuring layout was designed to allow the fibrous network to be exposed to the mercury atoms as delivered into the sensor chamber.

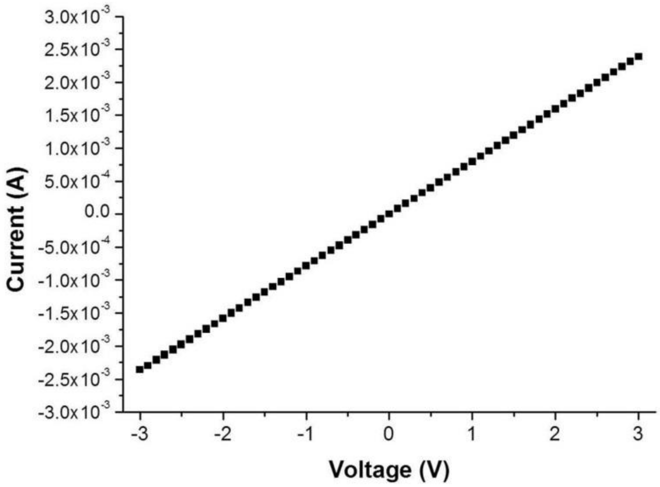

Figure 6. Chemosensor current-voltage curve

Sensing measurements, i.e. the current (or resistance) changes, were carried out in a continuous mode. The sensor measurements resulted in a change of the whole current (or resistance, i.e. I =V/R) according to Ohm's law. Firstly, the sensor was exposed to a flow of Hg^0 in air with a concentration of 800 ppb$_v$ for 1 min (Fig. 7, *right*), and then air was flowed through the measuring chamber to clean the sensor surface. A rapid decrease in current was recorded (1.056·10^{-7} A·s^{-1}) when Hg^0 entered the measuring chamber. The current curve trend slightly changed when clean air entered, quickly stabilizing to about the same current values reached for Hg^0 adsorption. Such an effect was probably due to the Hg^0 still housed inside the delivering tubes. The polluted line contribution was confirmed by further measurements (data not shown), where the slow current decrease completely disappeared when clean air never passed through part of tubes that had carried Hg vapors. Due to the strong affinity between Au and Hg^0, a 3 min-thermal treatment was necessary to remove mercury from layer and get the same starting current value.

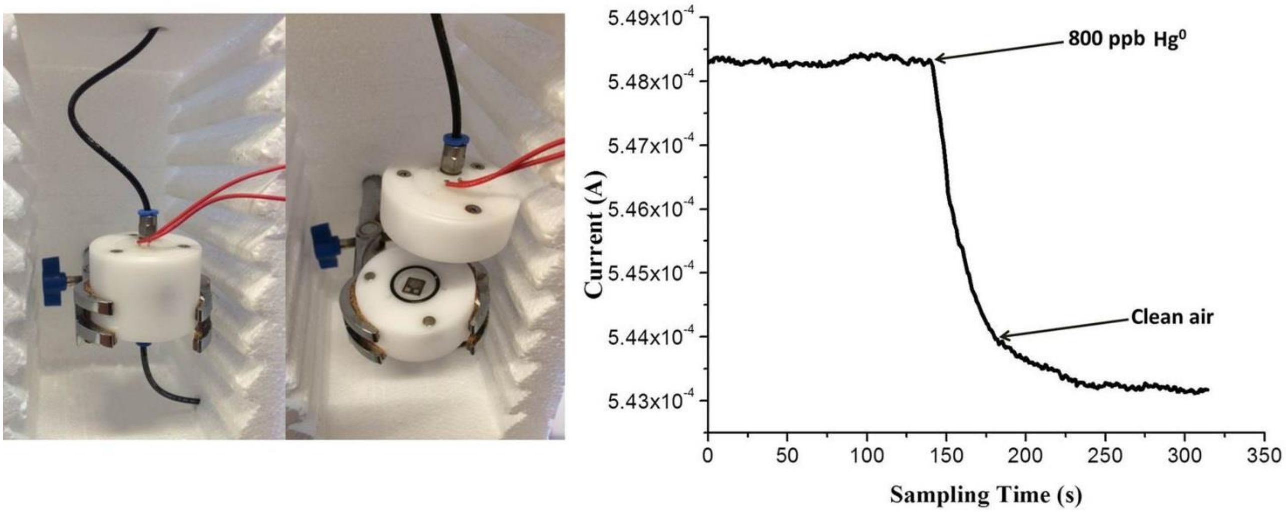

Figure 7. Homemade measurement chamber to house the chemosensor for laboratory experiments (left); plot depicting the transient response curve to 800 ppb Hg^0 (V=0.3 V)

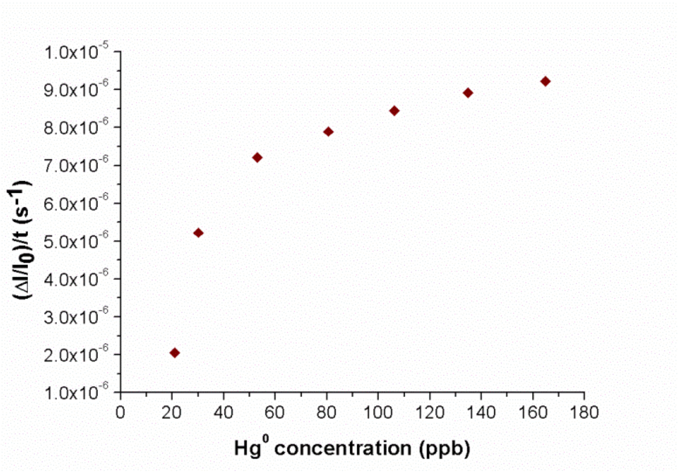

Figure 8. The normalized sensor response rate to the increasing concentration of vapour elemental mercury

Figure 8 depicts the normalized sensor response rate, i.e. the normalized current change per second, toward the increasing concentration of GEM (ranging between 20 and 160 ppb$_v$). Within this study, the selected flow rate was kept at 50 sccm in order to avoid turbulence effects. The resulting logarithmic curve describes the relationship between Hg^0 concentration and the response time: small variations of Hg^0 concentration up to 80 ppb$_v$ were able to deeply change the response rate, on the contrary higher concentration seemed to affect only weakly this sensing feature. Thus, since a strong relationship is recorded between the concentration and the response time under 80 ppb$_v$ of mercury, it is possible to find a correlation between the slope of the transient responses within the early minutes of the sensor response and well definite concentrations of Hg^0 in air. Figure 9 depicts the linear fitting of 10 min-sensor responses when increasing concentrations of mercury were flowed over the sensor. Related data were reported in Table 1.

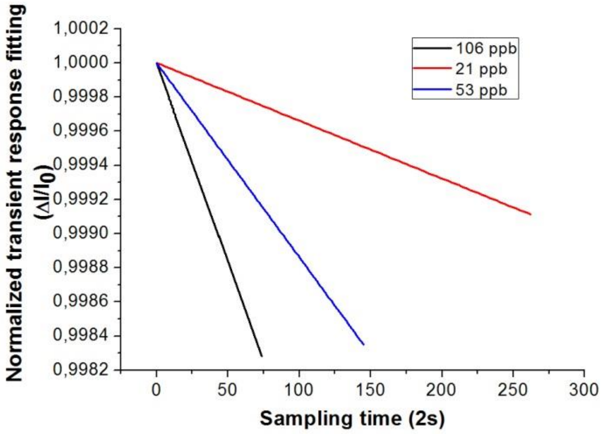

Figure 9. Linear fitting of the normalized sensor response within the first ten minutes

Table 1. Linear fitting parameters of 10 min-sensor responses to 21 ppb≤ [Hg^0] ≤106ppb

ppb$_v$	**($\Delta I/I_0$)s^{-1}**	**SE (±)**	**R^2**
21	-7.12602E-10	1.75521E-11	0.86
33	-1.50647E-9	1.05521E-10	0.91
39	-1.78067E-9	1.02615E-10	0.91
40	-1.85901E-9	1.01833E-10	0,92
53	-2.44657E-9	4.24993E-11	0.91
70	-3.19082E-9	2.55882E-11	0.93
106	-4.83599E-9	2.67462E-10	0.88

A linear relationship has been reported between the response rate and the concentration of Hg, according to the following equation (1):

$$(1) \qquad y = (-4.56226E^{-11}) \cdot [Hg^0],\ [Hg^0] < 100\, ppb;\ SE: \pm 1.504E^{-12};\ R^2 = 0.99675$$

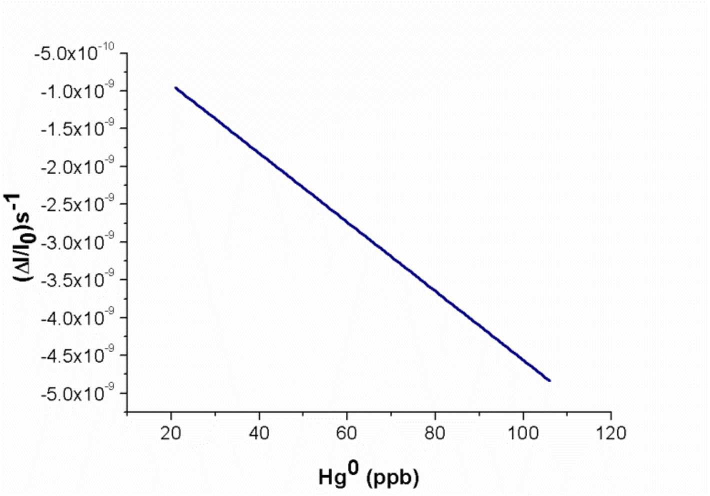

Figure 10. Linear relationships between the normalized response time and the Hg^0 concentration, within the range of 20 and 100 ppb_v.

Therefore when the concentration of Hg increased, the response curve slope changed too linearly, allowing a limit of detection of about 1 ppb_v for a 10 min-exposure (50 sccm). About main interfering compounds, since at room temperature and in dark condition the measured current is supposed to be due to AuNPs decorating titania fibers, only chemical compounds interacting with gold are expected to be mostly responsible of the current changes (i.e. halides and sulphides). Thus in a blend of other chemicals, this sensor has been designed as a pretty selective sensor, being able to greatly decrease the environmental disturbances allowing the investigator/manufacturer to design and then fabricate easier strategies to prevent contaminations from environment (selective filtering systems or coatings). Among common potential contaminants authors investigated previously water vapour influence (%RH) reporting no-effects on the electrical signals **(**Macagnano et al., 2015**)**.

4 Conclusions

The adopted sensing strategy has focused on the strong affinity of mercury to gold combined to the nanostructures properties. Exploiting the photocatalytic properties of electrospun titania nanofibers, a novel conductometric sensor has been designed and fabricated to detect GEM in air. Electrospinning technology has been used successfully to create a 3D-framework of titania covering the electrode sensing area of the properly designed chemoresistors (IDEs). Exploiting the photocatalytic properties of titania AuNPs have been grown on nanofibers. Such a sensor was able to work at room temperature and was sensitive to Hg^0 also after a few minutes of exposure to polluted air. Since it is composed of titania and gold, it sounds to be robust and resistant to common solvents and VOCs commonly in the air (as reported by literature). Preliminary results suggest that the short thermal treatments, necessary to desorb mercury from AuNPs, didn't seem to affect the electrical properties of the device. Depending on the strategy of sampling, a sensing device based on such a chemosensor, could be designed for real applications, specifically for real time monitoring of polluted sites. Few minutes of air sampling are sufficient to quantify the concentration of mercury in the air, in the range between 20-100 ppb_v (LOD: 1 ppb), without using traps or gas carriers. Changing parameters as the flow rate and the density and size of gold particles are expected to be significant parameters to improve the LOD and the response time, respectively. Finally, a modified transducer layout could be designed to exploit better the adsorptive capacity of the 3D-nanofibrous framework. However further investigations are necessary also to assess the effects of physical parameters of the environment, such as temperature fluctuations and UV-light (that should activate titania surface in adsorbing oxidized Hg), as well as chemical ones, such as volatile organic compounds and gas (like halides and sulphides) which are well known interfering of the adsorption process of the Hg^0 on gold.

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