

# Ultrasensitive mercury sensors based on graphene decorated with nanoparticles

Ahmad I. Ayesh<sup>a</sup>, Zainab Karam<sup>b</sup>, and Falah Awwad<sup>c</sup>

<sup>a</sup> Department of Math., Stat. and Physics, Qatar University, Doha, Qatar, [ayesh@qu.edu.qa](mailto:ayesh@qu.edu.qa)

<sup>b</sup> Masdar Institute, Abu Dhabi, United Arab Emirates

<sup>c</sup> Department of Electrical Engineering, United Arab Emirates University, Al Ain, United Arab Emirates

## ABSTRACT

In this work we present a highly sensitive and selective sensor for detection of mercury traces in water. The sensor is constructed by creating interdigitated metal electrodes on a graphene layer placed on SiO<sub>2</sub>/Si substrate. Nanoparticles were generated by sputtering and inert gas condensation inside an ultra-high vacuum system, and they were deposited on top of the graphene layer with the metal electrodes. The nanoparticles used in this work are gold (Au) because of their strong affinity to mercury. The sensor was tested by measuring the change in the electrical resistance of the sensor against different concentrations of Hg<sup>+2</sup>. The results demonstrate that the sensor can detect very low concentration of Hg<sup>+2</sup> (as low as 0.05ppb) which is much below the guideline value from World Health Organization (WHO). The fabricated sensor is functional at room temperature, and it has low power requirement. Therefore, the fabricated sensor has potential to be used for practical applications related to water quality.

**Keywords:** mercury sensor, graphene, nanoparticles, gold, inert-gas condensation

## 1 INTRODUCTION

Mercury II (Hg<sup>+2</sup>) is a highly toxic heavy metal ions and neurotoxicant [1]. Exposure to Hg<sup>+2</sup> would result in kidney and respiratory failure, as well as damage in the gastrointestinal tract and in the nervous system [2]. The amount of Hg<sup>+2</sup> released yearly into water resources by human activities is about 10,000 tons [3], this causes a severe threat on human life. Therefore, a fast, accurate, and reliable measure of the level of mercury has become increasingly important for public security and health protection.

A chemical sensor is a device that produces a response upon exposure to a chemical that introduces functionally related output. The response is an alert in one or more of the sensor properties such as: mass, electrical conductivity, capacitance, etc. Conductometric (or resistive) sensors have attracted significant interests for trace analysis of heavy metals because of their excellent sensitivity, short analysis time, low power consumption, and cheap equipment [4]. However, many chemical sensing systems have not yet reached commercial viability because of their limited 3S-drawbacks (sensitivity, stability, and selectivity). Thus, suitable sensor materials with the required surface, bulk

properties, sensitivity, stability, and selectivity are currently needed. In recent years, nanotechnology-based sensors technique has become one of the most active areas in environmental analysis [5]. Nanoclusters are small particles of 2 to about 105 atoms which bridge the gap between quantized states in atoms and molecules on one side and continuous states in the bulk on the other side. Many of the new properties which appear for a material as its size is reduced to a nanosize can be assigned to the dominance of quantum effects at small scales and the influence of the surface of nanoclusters. The number of atoms on the surface of a bulk material is negligible compared to the total number of atoms inside the material. However, the fraction of surface atoms becomes important for nanoclusters. The large number of surface atoms makes nanoclusters suitable candidates for sensing applications. In addition, nanoclusters have unique capabilities, such as increased mass transport, low detection limit, and better signal-to noise ratio.

Among many conductometric sensors so far reported for detecting Hg<sup>+2</sup>, gold was found to be a superior material because of its strong affinity to mercury which could enhance the preconcentration effect [6,7]. Thus, Au nanoclusters can be used for Hg<sup>+2</sup> sensing applications with high sensitivity, where they behave as a modifier due to their large ratio of surface atoms and strong affinity between Au and Hg. For instance, Compton et al. loaded Au nanoclusters onto glassy carbon microspheres and then electrically wired the Au-modified glassy carbon microsphere film to the underlying macroelectrode using carbon nanotubes [8]. Raj et al. constructed Au nanocluster based ensembles onto the thiol functionalized sol-gel silicate network by a colloidal chemical approach [9].

Graphene is a monolayer sheet of carbon atoms packed into a two-dimensional (2D) honeycomb lattice that has exceptional thermal and mechanical properties, as well as high electrical conductivity. Graphene also provides potential applications in synthesizing nanocomposites, nanoelectronics, electromechanical resonators, and ultrasensitive sensors [10]. Graphene possesses excellent electrochemical catalytic activity, and it is a novel material with excellent performance for sensor applications. The mechanism of action for graphene based sensors is that chemical species adsorbed on the surface of the graphene act as electron donors or acceptors, resulting in conductance changes.

Different chemical sensors were fabricated recently using graphene-based materials such as electrochemical

determination of capillary glucose concentration [11], nicotinamide adenine dinucleotide [12], dopamine [13], cytochrome c [14], and DNA biosensors [15]. Graphene-based materials hold great promise on fabricating enhanced chemical-sensing platforms.

The above studies demonstrate that graphene has emerged as a promising material for sensors [8]. However, many of the interesting and unique properties of graphene can only be realized after it is integrated into more complex assemblies. Herein, graphene should be incorporated with a material that is sensitive and selective for the chemical to be detected ( $\text{Hg}^{+2}$  in the present work). Thus, the incorporation of Au nanoparticles with graphene is an excellent choice for devices that are designed for  $\text{Hg}^{+2}$  sensing applications. However, graphene-based nanocomposite film has been rarely used for the sensing the  $\text{Hg}^{+2}$  traces [16]. In addition, the integration of Au nanoparticles that are fabricated using sputtering and inert gas aggregation within graphene based sensors for the detection of  $\text{Hg}^{+2}$  traces in water had not been reported, to the best of our knowledge. This method of nanocluster production involves many advantages. The main advantage of this technique is the precise control of the nanoparticle size which can be utilized to enhance the sensitivity of nanoparticles for  $\text{Hg}^{+2}$  detection [14]. Also, the prepared nanoclusters are of high purity since they are prepared inside an ultra-high vacuum (UHV) system. In addition, this kind of nanoclusters prepared inside an UHV system can be self-assembled directly on the device without the need for any additional experimental steps. On top of the previous advantages, sputtering is a reliable technique that is adopted by industry for mass production of metal with reliable cost. Thus, our approach for the production of Au nanoparticles can be adopted by industry.

We demonstrates the fabrication of sensors for the detection of  $\text{Hg}^{+2}$  traces in water using Au nanoparticles and graphene layers. The combination between Au nanoclusters and graphene utilizes the advantages of both nanostructures and graphene which greatly facilitate electron-transfer processes and the sensing behavior for  $\text{Hg}^{+2}$  detection, leading to a remarkably improved sensitivity and selectivity.

## 2 EXPERIMENTAL

A magnetron sputtering aggregation source was utilized to synthesize Au nanoparticles inside the UHV compatible system, shown in Fig. 1[15]. The dc magnetron discharge was utilized to generate nanoclusters from Au target. Argon (Ar) gas with 99.999% purity was used to create the plasma which sputters the material and aggregates Au nanoparticles. The target and the magnetron gun are mounted on a motorized linear translator that allows varying the distance from the sputtering target to the source exit nozzle (aggregation length,  $L$ ) up to 100 mm. A quadrupole mass filter (QMF) is located at the exit of the source chamber (see Fig. 1) to measure the nanoparticle

size distribution before deposition. Herein, nanoparticle size refers to the nanocluster diameter assuming spherical nanoparticles. The QMF consists of four parallel metal rods where each pair of opposite rods is connected together electrically to potentials of  $(U+V\cos(\omega t))$  and  $-(U+V\cos(\omega t))$  respectively ( $U$  is a dc voltage and  $V\cos(\omega t)$  is an ac voltage). The resolution of the filter was adjusted for a size scan by setting the  $U/V$  ratio up to 0.168.

A Faraday cup located at the exit of the mass filter has been utilized to measure the ion flux of the selected size nanoclusters [16].

Each  $\text{Hg}^{2+}$  sensor was fabricated using (1 cm X 1cm) commercial graphene layer on  $\text{SiO}_2/\text{doped-Si}$  substrate (thickness of  $\text{SiO}_2$  is 285 nm, and Si is p-type with resistivity of 0.001-0.005 ohm.cm). Interdigitated parallel Au electrodes (with electrode separation of 100  $\mu\text{m}$ ) were fabricated by thermal evaporation using a Torr International evaporator through a shadow mask on the surface of graphene, as shown in the inset of Fig. 1 [17]. Two batches of sensors were tested in this work: i) sensors based on graphene only, and ii) sensors based on graphene and percolating films of Au nanoparticles, each has a thickness of 5.

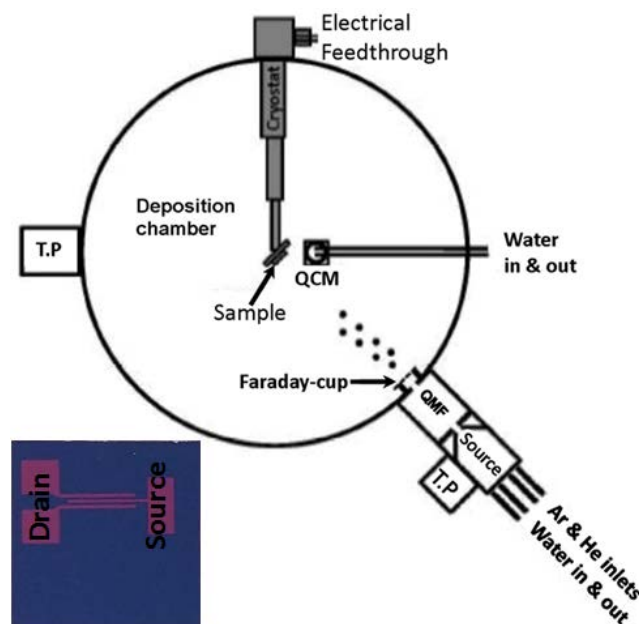


Fig. 1 Schematic diagram of the UHV compatible system and nanoparticle deposition [15]. The inset is an image of the graphene sample.

## 3 RESULTS AND DISCUSSION

Inset (a) of Fig. 2 shows the response electrical current of the sensor based on graphene when exposed to 0.05ppb of  $\text{Hg}^{2+}$  solution. The figure reveals reasonable variation in the electrical current when exposed to  $\text{Hg}^{2+}$ . The response of the present sensor based on graphene for  $\text{Hg}^{2+}$  stimulant

is nearly instantaneous. The decrease in the electrical current of the sensor when exposed to  $\text{Hg}^{2+}$  can be assigned to the adsorption of  $\text{Hg}^{2+}$  on surface of the sensor. Herein, the accumulation of positive charges from  $\text{Hg}^{2+}$  ions decreases electron concentration in n-type graphene and increases holes concentration which in turn decreases the electrical current.

Figure 2 demonstrates the dependance of the electrical current signal of the current sensor based on graphene when exposed to different concentrations of  $\text{Hg}^{2+}$  solution. This figure demonstrates that increasing the concentration of  $\text{Hg}^{2+}$  decreases the electrical current signal. This behavior has been observed before in [18], and can be explained as result of the increase in the p-doping effect because of the absorption of  $\text{Hg}^{2+}$  on the channel.

For sensors based on graphene and Au nanoparticles, the nanoparticles were produced using a discharge power of 21 W, inert gas flow rate of 40 sccm, and aggregation length of 60 mm. The size distribution of Au nanoparticles used in this work as measured using QMF is shown in inset (b) of Fig. 2. The figure reveals narrow size distribution, and an average nanocluster size of  $6.82 \pm 0.30$  nm.

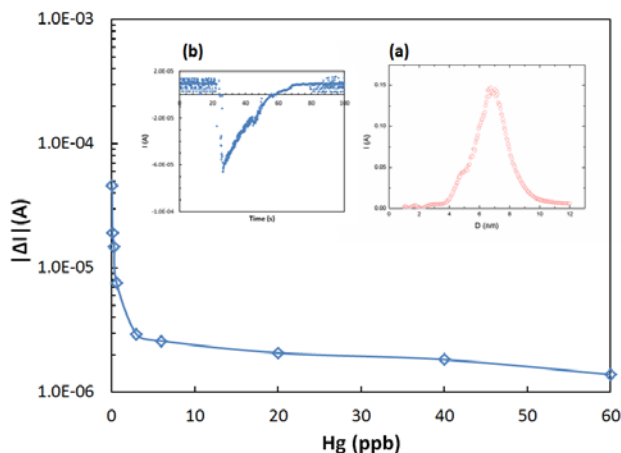


Fig.2 Response signal of graphene sensor based on graphene when exposed to  $\text{Hg}^{2+}$  solutions with different concentrations. Inset (a) Response electrical current of the sensors when exposed to 0.05 ppb  $\text{Hg}^{2+}$  solution. (b) Size distribution of gold nanoparticles used in this work as measured using QMF. Inset.

Figure 3 shows the electrical response of the present sensors when exposed to 0.6 ppb solution of  $\text{Hg}^{2+}$  ions. The figure reveals that the fabricated sensors with Au nanoparticles are more sensitive to  $\text{Hg}^{2+}$  ions than those with graphene only. The more significant decrease in electrical current for sensors with Au nanoclusters can be assigned to additional adsorption of  $\text{Hg}^{2+}$  on Au nanoclusters due to their high affinity to Au.

## 4 SUMMARY

Conductometric sensors based on graphene and gold nanoparticles that can be utilized for detection of mercury ions ( $\text{Hg}^{2+}$ ) were presented in this work. Graphene on a  $\text{SiO}_2/\text{doped-Si}$  substrate was used for the sensor. Interdigitated electrodes were deposited on the surface of graphene followed by self-assembly of gold nanoparticle percolating film. The sensors were highly sensitive for  $\text{Hg}^{2+}$  (0.05 ppb). The sensitivity of the present sensors is below the minimum allowed limit of  $\text{Hg}^{2+}$  in drinking water set by the World Health Organization and that set by the United States Environmental Protection Agency. These sensors are small in size and easy to carry outdoor and have low power requirements, thus, they have a potential to be used for practical field applications.

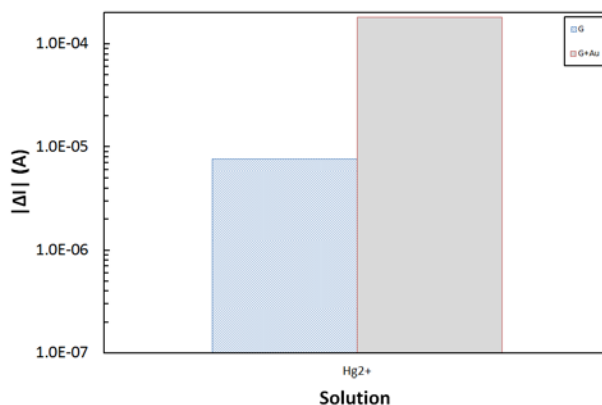


Fig.3 Comparison between the sensitivity of the current sensors (based on graphene only, or graphene and Au nanoparticles) when exposed to solutions with different metal ions with a concentration of 0.6 ppb.

## 5 ACKNOWLEDGMENTS

This work was supported by the United Arab Emirates University fund number 31R006.

## REFERENCES

- 1) P.B. Tchounwou, W.K. Ayensu, N. Ninashvili, D. Sutton, Review: environmental exposure to mercury and its toxicopathologic implications for public health, Inc., Environ. Toxicol. 18 (2003) 149–175.
- 2) G.E. McKeown-Eyssen, J. Ruedy, A. Neims, Methyl mercury exposure in northern Quebec: II. Neurologic findings in children, Am. J. Epidemiol. 118 (1983) 470–479.
- 3) Katalyse Umweltgruppe e. V. Chemie in Lebensmitteln, Zweitausendeins: Frankfurt, Germany, Chapter 2, 1981.
- 4) D.W. Pan, Y. Wang, Z.P. Chen, T.T. Lou, W. Qin, Nanomaterial/ionophore-based electrode for anodic

- stripping voltammetric determination of lead: an electrochemical sensing platform toward heavy metals, *Anal. Chem.* 81 (2009) 5088–5094.
- 5) X.L. Hu, G.S. Li, J.C. Yu, Design, fabrication, and modification of nanostructured semiconductor materials for environmental and energy applications, *Langmuir* 26 (2010) 3031–3039.
  - 6) O. Ordeig, C.E. Banks, J. del Campo, F.X. Muñoz, R.G. Compton, Trace detection of mercury(II) using gold ultra-microelectrode arrays, *Electroanalysis* 18 (2006) 573–578.
  - 7) P. Miao, L. Liu, Y. Li, G. Li, *Electrochem. Commun.* 11 (2009) 1904–1907.
  - 8) X. Dai, G.G. Wildgoose, C. Salter, A. Crossley, R.G. Compton, Electroanalysis using macro-, micro-, and nanochemical architectures on electrode surfaces, bulk surface modification of glassy carbon microspheres with gold nanoparticles and their electrical wiring using carbon nanotubes, *Anal. Chem.* 78 (2006) 6102–6108.
  - 9) B.K. Jena, C.R. Raj, Gold nanoelectrode ensembles for the simultaneous electrochemical detection of ultratrace arsenic, mercury, and copper, *Anal. Chem.* 80 (2008) 4836–4844
  - 10) J.D. Fowler, J.M. Allen, V.C. Tung, Y. Yang, B.H. Weiller, Practical chemical sensors from chemically derived graphene, *ACS Nano* 3 (2009) 301–306.
  - 11) T.T. Baby, S.S. Jyothirmayee Aravind, T. Arockiadoss, R.B. Rakhi, S. Ramaprabhu, Metal decorated graphene nanosheets as immobilization matrix for amperometric glucose biosensor, *Sens. Actuators B* 145 (2010) 71–77.
  - 12) W.J. Lin, C.S. Liao, J.H. Jhang, Y.C. Tsai, Graphene modified basal and edge plane pyrolytic graphite electrodes for electrocatalytic oxidation of hydrogen peroxide and b-nicotinamide adenine dinucleotide, *Electrochem. Commun.* 11 (2009) 2153–2156.
  - 13) Y. Wang, Y. Li, L. Tang, J. Lu, J. Li, Application of graphene-modified electrode for selective detection of dopamine, *Electrochem. Commun.* 11 (2009) 889–892.
  - 14) J.F. Wu, M.Q. Xu, G.C. Zhao, Graphene-based modified electrode for the direct electron transfer of cytochrome c and biosensing, *Electrochem. Commun.* 12 (2010) 175–177.
  - 15) A. I. Ayesh, S. Thaker, N. Qamhieh, and H. Ghamlouche, *J. Nanopart. Res.* 13, 1125 (2011).
  - 16) A. I. Ayesh, N. Qamhieh, H. Ghamlouche, S. Thaker, and M. EL-Shaer, *J. Appl. Phys.* 107, 034317 (2010).
  - 17) A.I. Ayesh. Electronic transport in Pd nanocluster devices, *Applied Physics Letters* 98 (2011) 133108.
  - 18) Z. Yin, Q. He, X. Huang, J. Zhang, S. Wu, P. Chen, G. Lu, P. Chen, Q. Zhang, Q. Yan, H. Zhang. Real-time DNA detection using Pt nanoparticle-decorated reduced graphene oxide field-effect transistors, *Nanoscale* 4 (2012).