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Fabrication of Selective Sensors for Hg²⁺ Traces in Water Using Graphene Decorated with Metal Nanoclusters

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Mercury metal is released into water by different sources including sewage industrial waste, thus, it can enter human food chain. It is considered one of the most harmful pollutant of heavy metals since it is non-biodegradable, and it can enter to human body by different means including direct consumption (for example, through drinking water), absorption through skin, and by respiratory system. Exposure to mercury cause severe effects on human health such as brain damage, kidney failure, damage in the nervous system, birth defects, chromosome breakage, and paralysis [1, 2]. The United Nation Environment Program (UNEP) assessed the annual released quantity of mercury to 4400–7500 tons [3]. In addition, the International World Health Organization regulated the maximum allowed amount of mercury ions (Hg²⁺) in drinking water to 6 ppb [4]. Nevertheless, previous studies estimated the allowed amount of inorganic Hg²⁺ in water to 0.5 ppb [5]. Therefore, the development of sensitive, selective, reliable, and cost effective Hg²⁺ sensors is needed for medical diagnostic, quality control of food industry, as well as water and environment quality monitoring. In this work, we present novel conductometric sensors based on graphene and Au nanoclusters that are highly selective to Hg²⁺ ions. Electrical electrodes were deposited on the surface of graphene by thermal evaporation. Au nanoclusters were produced by sputtering and inert gas condensation technique inside an ultra-high vacuum chamber, and they were self-assembled on the surface of graphene. To the best of our knowledge, the sensors reported here are the first conductometric sensors based on graphene and Au nanoclusters that are utilized for detection of Hg²⁺ traces in water. These sensors were exceedingly sensitive to Hg²⁺ ions, therefore, they have potential to be applied for practical life applications. Gold nanoclusters were produced by the sputtering and inert gas condensation technique inside an ultra-high vacuum system. The system consists of three main chambers (source, mass filter, and deposition chambers) that were pumped initially to a base pressure of 10⁻⁸ mbar using two turbo pumps. A gold target of purity 99.99% (Testbourne Ltd, UK) was fixed on a water-cooled magnetron sputter

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head. Plasma was generated inside the source chamber using argon (Ar) inert gas, and it was used to sputter Au from its target through dc discharge type. The supplied Ar gas was also utilized to condense the sputtered material forming nanoclusters, and to create pressure gradient between the source and deposition chambers that enables the formed nanoclusters to travel to the deposition chamber. Each Hg^{2+} sensor was fabricated using (1 cm \times 1cm) commercial graphene layer on SiO_2 /doped-Si substrate (thickness of 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 μm) were fabricated by thermal evaporation using a Torr International evaporator through a shadow mask on the surface of graphene [6]. 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 nanoclusters, each has a thickness of 5 nm. For nanocluster deposition, each graphene sample was fixed on a cryostat finger. Nanocluster deposition rate was initially measured using a quartz crystal monitor (QCM) facing nanocluster beam and was fixed on a motorized linear translator. Next, the QCM was removed away from the sample, thus, nanoclusters were deposited on graphene surface. Sensitivity measurements were performed using Hg^{2+} solutions with different concentrations (0.05, 0.1, 0.3, 0.6, 3, 6, 20, 40, and 60 ppb). The selectivity was tested using 0.6 ppb solutions of the following ions: Cr^{2+} , Cd^{2+} , Cu^{2+} , Co^{2+} , Fe^{2+} , Zn^{2+} , and K^+ . The selectivity results of the sensor reveal that the fabricated sensors are selective to Hg^{2+} ions, and the selectivity is evidently enhanced for sensors with Au nanoclusters. The sensitivity of sensors decorated with Au nanoclusters to Hg^{2+} ions is higher than that for sensors made of graphene only, which could be assigned to the high binding affinity of Au nanoclusters to Hg^{2+} ions [7, 8]. This can be explained qualitatively bearing in mind previous studies that investigated the binding energy of the metal ions (under consideration in this work) with either graphene or Au nanoclusters. Upon investigating the binding energy of metal ions with graphene, it was reported that Hg^{2+} ions have the highest binding energy to graphene compared to other ions (Cr^{2+} , Cd^{2+} , Cu^{2+} , Co^{2+} , Fe^{3+} , Zn^{2+} , and K^+), which exhibit slightly lower binding energy to graphene and thus their sensitivity signals are very comparative [8]. The sensitivity of Au nanostructures to Hg^{2+} ions was found to be large due to their high binding energy [7]. In addition, the binding energy of Hg^{2+} ions to Au nanostructures is evidently higher than that to the other metal ions investigated in this work [9], which makes the graphene-Au sensor selective to Hg^{2+} ions. The sensing mechanism of the graphene-based sensors can be summarized as follows: exposure of the graphene sensor to Hg^{2+} ions decreases electron concentration in the n-type graphene, thus, the conductance of the sensor decreases. Decoration of graphene with Au nanoclusters creates electron scattering centers that increase electron diffusive scattering which decreases electrical conductance. Adsorption of Hg^{2+} ions on Au nanoclusters causes further decrease in the conductance, which implies the increase in the sensitivity and selectivity of the sensor. In conclusion, the sensitivity of the present sensors is below the minimum allowed limit of 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.

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