A paper-based inkjet-printed PEDOT:PSS/ ZnO sol-gel hydrazine sensor

Tutku Bedük^a, Eloise Bihar^{a,b}, Sandeep G. Surya^a, Aminta Naidili Castillo Robles^a, Sahika Inal^b, Khaled Nabil Salama^{a,*}

^a*Sensors Lab, Advanced Membranes and Porous Materials Center, Computer, Electrical and Mathematical Science and Engineering Division, King Abdullah University of Science and Technology (KAUST), Thuwal 23955-6900, Saudi Arabia*

^b*Organic Bioelectronics Lab, Division of Biological and Environmental Science and Engineering, King Abdullah University of Science and Technology (KAUST), Thuwal 23955, Saudi Arabia*

*Corresponding author.

E-mail address: khaled.salama@kaust.edu.sa; Phone: +9662-808-4420

Graphical abstract

Highlights

- The preparation of fully inkjet printed PEDOT:PSS electrodes on commercial printing paper followed by inkjet printing of ZnO sol-gel
- A paper based electrochemical sensor for hydrazine sensing with a good selectivity and reproducibility
- Sensitivity comparison of PEDOT:PSS/Nafion and PEDOT:PSS/ZnO/Nafion sensors
- Characterization of PEDOT:PSS and ZnO through SEM, XPS and AFM
- Excellent detection in mineral water and seawater samples with a recovery of 98.7 to 104.2 % respectively.

ABSTRACT

Hydrazine is widely used in industries as a precursor for blowing agents, pharmaceuticals, and pesticides. It is a highly toxic compound; therefore, it is of paramount interest to develop new analytical methods for the detection and control of hydrazine exposure. In this work, we describe the fabrication of an all inkjet-printed paper sensor composed of poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) electrode functionalized with zinc oxide (ZnO) and encapsulated in a Nafion matrix for the amperometric determination of low concentrations of hydrazine. The electrochemical properties of the fully inkjet-printed PEDOT:PSS/Nafion and PEDOT:PSS/ZnO/Nafion sensors are compared in the presence and absence of different concentrations of hydrazine. The stability and sensitivity of these electrodes are significantly enhanced after modification with ZnO particles. The layer-by-layer deposition of the materials on the electrode surface is characterized by SEM, XRD, and AFM. The printed sensor exhibits a linear response in the 10 to 500 μM hydrazine concentration range and a ~ 5 μM detection limit (at $S/N = 3$). The electrochemical sensitivity is $0.14 \mu\text{A} \cdot \mu\text{M}^{-1} \cdot \text{cm}^{-2}$, and the best working voltage is 0.5 V. The developed sensor was applied successfully for the determination of hydrazine content in tap, sea, and mineral water samples validating the accuracy of this sensor.

Keywords: Inkjet Printing, paper electronics, zinc oxide, sol-gel, point-of-care sensor, PEDOT:PSS, hydrazine sensor

1. Introduction

Hydrazine is a highly toxic, colorless reducing agent and flammable liquid, only stable when handled as a solution. According to the Environmental Protection Agency (US EPA) and the National Institute for Occupational Safety and Health (NIOSH) USA, hydrazine is a carcinogenic, mutagenic, and hepatotoxic neurotoxin, immunotoxin, and genotoxic environmental pollutant in ppm levels [1, 2]. High-level hydrazine exposure can act as a convulsant for the human central nervous system (CNS). At lower doses of hydrazine, the CNS can be depressed, and nose, throat, and eye irritation may occur [3]. The toxicity of multiple low doses has cumulative effects. Previous studies reveal that hydrazine has a poisonous effect that causes alopecia and damages lungs, liver, and kidneys in exposed animals [4]. However, hydrazine still has numerous applications in pharmaceutical, agricultural, military, and chemical industries worldwide. It is used in the synthesis of rocket fuels, explosives, blowing agents, antioxidants, fungicides, herbicides, insecticides, and pharmaceuticals [5]. Therefore, the development of easy-to-use, inexpensive, and efficient methods for sensitive and selective detection of hydrazine is important to monitor and minimize exposure of humans and the environment [6-8].

Conventional analytical techniques are used for hydrazine detection, such as spectrophotometry, chromatography, or electrochemical methods [9-11]. However, most of the commercial tools are extremely complex and exhibit low precision, although the electrochemical method of hydrazine detection offers simplicity, low cost, and rapid processes [12]. In addition, electrochemical digital signal read-out platforms are more robust than spectrophotometric detection methods and the detection system is suitable for miniaturization. A common approach is the deposition of nanomaterials such as metal oxides or metal/metal oxide composites onto a conductive electrode surface. This technique is widely used for biosensor development as it enhances the surface area of the electrode as well as improves the device performance for the detection of environmental

pollutants [13, 14]. Indeed, nanomaterials have superior properties as compared to their bulk substances, such as mechanical strength, thermal stability, catalytic activity, electrical conductivity, magnetic properties, and optical properties. For instance, ZnO-based electrochemical sensors are reported many times in the literature because of their excellent stability, electrochemical activity, and ability to improve electron exchange with higher specific-surface areas.[15-19].

Conducting polymers have been widely studied for sensing applications due to their ease of processing, high conductivity, and biocompatibility. Among them, poly(3,4- ethylenedioxythiophene) doped with poly(styrene sulfonate) (PEDOT:PSS) is a promising material because of its soft nature, mixed electronic/ionic conductivity, and printability [20]. It is also suitable for the deposition onto cheap and eco-friendly paper substrates, which provides a good opportunity for constructing disposable bio-friendly biosensors [21, 22]. Only a few studies report the use of electrochemical sensors utilizing PEDOT:PSS electrodes for the detection of hydrazine [23]. Tolstopjatova et al. describe two methods for the preparation of Palladium (Pd)/PEDOT:PSS polymer composite electrodes for hydrazine detection. The first one is the synthesis of PEDOT films electrodeposited from an EDOT solution in acetonitrile under galvanostatic conditions with a potential range of 1.3–1.0 V. The second is drop casting of Pd(II) and PEDOT:PSS mixture onto the glassy carbon electrode surface after the spontaneous reduction of Pd(II) in contact with PEDOT:PSS with a water dispersion. They show that Pd nanoparticles catalyze the oxidation of hydrazine, and catalytic performance is increased by Pd particles coverage [23]. A drawback is the complexity of the electrode fabrication method and the reaction processes. Contrary to lithography or electropolymerization, inkjet printing technology offers a simple fabrication route without the use of masks and with a chance of scaling up. The ease of the inkjet printing technology provides a promising electrode fabrication method for various kinds of materials and substrates. Being cost and time effective is a crucial step for the fabrication of disposable sensors. Solution processing technologies (spraying techniques, screen-printing or inkjet printing etc) are very practical due to the straightforward fabrication steps. Furthermore, inkjet printing allows the digital fabrication of customizable designs at atmospheric conditions. It is possible to modify the patterns on demand, which is a key of fabricating diagnostic

devices on various flexible substrates successfully. The geometry as well as thickness of the printed pattern can be easily controlled during the printing process. Furthermore, the wastage created by inkjet printing is reduced compared to other fabrication methods, and the inks can be deposited at room temperature [24, 25].

To best of our knowledge, no study has ever reported inkjet-printing for the realization of hydrazine sensors and no study has ever proposed the combination PEDOT:PSS/ ZnO to detect hydrazine. We report the fabrication of all inkjet-printed, ZnO sol-gel modified PEDOT:PSS/Nafion electrodes for hydrazine detection using a commercial paper as an eco-friendly and recyclable substrate. We show, for the first time, that printing ZnO sol-gel onto PEDOT:PSS electrodes improves the performance of the working electrode in terms of sensitivity and selectivity toward hydrazine detection. We also demonstrate that adding an encapsulation layer, Nafion, printed onto the working area of the sensor improves stability and provides protection to the electrode material. The key advantages of our work is that the developing paper based analytical device is affordable for extending remote sensing applications, low-weighted and useful for point of care applications. The paper-based systems are promising since they require minimal instrumentation and low power. Moreover, they can readily be embedded with microelectronics in a miniaturized chip-based format. This work represents a steppingstone for developing paper-based fully inkjet printed electroanalytical tools for hydrazine detection.

2. Experimental

2.1. Materials and reagents

PEDOT:PSS ink (CLEVIOSTMPJET700 N) was purchased from Heraeus.

Glycidoxypyriltrimethoxysilane (GOPS), dodecyl benzene sulfonic acid (DBSA), and Nafion 117 solution were purchased from Sigma Aldrich. Dielectric ink (EMD6200) was obtained from Sun Chemical. Nickel(II) nitrate hexahydrate ((Ni(NO₃)₂·6H₂O; ≥98.5%), sodium hydroxide (NaOH; ≥98)

pellets, hydrazine solution (35 wt%) in water, sodium chloride (NaCl; $\geq 99.5\%$), copper(II) sulfate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$; $\geq 98\%$), zinc acetate dehydrate, ethanolamine, 2-methoxyethanol, and methylhydrazine (98%) were purchased from Sigma-Aldrich. The phosphate-buffered saline (PBS) tablets containing 0.0027 M potassium chloride (KCl) and 0.137 M sodium chloride (NaCl) and KCl (certified ACS; 99.0-100.5%) were purchased from Fisher BioReagents. Potassium sulfate (K_2SO_4 ; powder/certified ACS) and Phenylhydrazine (97%) was purchased from Alfa Aesar (Thermo Fisher Scientific, Germany, <https://www.alfa.com>). The ultrapure water (resistivity, $18.2 \text{ M}\Omega \cdot \text{cm}$) from a Milli-Q® integral water purification system (Merck KGaA, Darmstadt, Germany) was used in all aqueous solution experiments. All the chemicals were of analytical grade and used as obtained.

2.2. Ink formulation

The preparation of PEDOT:PSS and Nafion solutions was based on a procedure reported by Bihar et. al [25]. Briefly, 1 wt% of GOPS and 0.4% v/v of DBSA were mixed with the PEDOT:PSS ink for 30 minutes in an ultrasonic bath and strained through a filter with a pore size of $1.2 \mu\text{m}$. GOPS was added as a crosslinker to improve the water stability of the ink. It also contributes to the homogeneity of the conducting mixture and wettability of the ink during printing. ZnO sol-gel was prepared by mixing zinc acetate dehydrate in $21 \mu\text{L}$ of ethanolamine and 1 mL of 2-methoxyethanol solution. As a final layer, 1% w/w solution of Nafion was prepared in deionized water and printed on top of the ZnO/PEDOT: PSS layers as encapsulation.

2.3. Inkjet printing

A Dimatix DMP-2800 inkjet-printer device was used for all fabrication steps of our sensors. As the first step, three layers of PEDOT:PSS ink were printed on commercial paper (ArjoWiggins) at 50°C with a drop spacing of $20 \mu\text{m}$. Printed PEDOT:PSS layers were dried on a hot plate for 30 minutes at 110°C . The geometrical area of the working space was 9.56 mm^2 . Secondly, two layers of ZnO sol-gel were printed on top of the working area by using a drop spacing of $30 \mu\text{m}$. Following printing, the working electrodes were cured on a hot plate at 150°C for 20 minutes. Then one layer of Nafion was printed on top of the sensing area. . The printing parameters (drop spacing and the number of printed

layers) selected for the study correspond to the best conditions for the deposition of uniform and homogeneous layers. For the sensor performance optimization, it was found that three layers of PEDOT:PSS, two layers of ZnO sol-gel and one layer of Nafion were optimum (Table S1, S2, S3, S4). Finally, to insulate the printed device, one layer of a commercial dielectric ink (EMD6200, SunChemical) was printed on top of the interconnects.

2.4. Characterization of the electrodes and electrochemical tests

Morphology of the printed PEDOT:PSS and ZnO inks was investigated using field emission scanning electron microscopy (FE-SEM, Carl Zeiss, Merlin). The X-ray diffraction data were recorded using X-ray diffractometer (Bruker Corporation, D8 ADVANCE, and Karlsruhe, Germany) with Cu K α radiation (1.5406 Angstrom). The intensity data were collected over a 2θ range of 20–80°. The difference between surface morphology and topography of PEDOT film before and after ZnO sol-gel modification and thicknesses was evaluated and determined using atomic force microscopy (AFM) (Bruker Dimension Icon with ScanAsyst®). The electrochemical tests were performed using an electrochemical measurement station (Palmsens, EmStat Blue). All the cyclic voltammetry measurements were performed in PBS (0.1 M, pH 7.4) with a scan rate of 50 mV/s. Cyclic voltammetry measurements were conducted in the voltage range of -0.2V to +0.6 V. Chronoamperometry measurements were performed at 0.5 V vs. PEDOT:PSS reference electrode.

2.5. Detection of hydrazine in real water sample

Tap water, seawater, and three different mineral water samples were spiked with 40 μ M and 100 μ M of hydrazine and analyzed under optimized conditions by using ZnO sol-gel modified PEDOT:PSS/Nafion sensors. Five mL of each liquid was collected and diluted to 10 mL with previously prepared 0.2 M of PBS. The seawater sample was centrifuged and filtered before use. After that, the spiked mixture was pipetted onto the device for chronoamperometry measurements. The statistical analyses of the data were conducted for the detection of hydrazine in water samples using the printed PEDOT:PSS/ZnO/Nafion sensor. The statistical differences between groups were determined by one-way ANOVA, with $p < 0.05$ being considered statistically significant.

Please insert Fig. 1. Here

3. Results and Discussion

3.1. PEDOT:PSS and PEDOT:PSS/ZnO sensor preparation and electrochemical properties

The schematic representation and photograph of the sensor layers, mass-produced inkjet printed devices as well as working, reference, and counter electrodes, are shown in Figure 1a, 1b and Figure S1 respectively. Besides the WE base, the auxiliary electrodes of this sensor are made of PEDOT:PSS. The ink was prepared from a commercially available PEDOT:PSS ink compatible with inkjet printing. We used the printing parameters optimized by Bihar et al. for the formation of a conductive and uniform PEDOT:PSS layer on paper [25]. Our assumption is that ZnO enhances the electrocatalytic activity of the sensor because of an increased surface area. The electrochemical oxidation of hydrazine is a four-electron transfer process that releases nitrogen gas as a final product (Figure 1a). It has been previously reported that the presence of zinc oxide particles promotes electron transfer on the substrate surface and enhances sensitivity toward hydrazine [26]. To encapsulate the active (sensing) layer, we printed one layer of Nafion on top of the working area. This permselective negatively charged layer creates good attachment to a positively charged ZnO surface. As seen in Figure 1c, the oxidation current, measured between 0.4 V and 0.6 V, of the PEDOT:PSS/ZnO/Nafion layer increases with stronger concentrations of hydrazine. An additional oxidation peak at 0.2 V and reduction peak at 0.1V corresponding to a redox couple of ZnO are observed in the cyclic voltammetry (CV) curve (Figure 1c). We compared the current responses of the sensors in the presence and absence of a Nafion layer (Figure S2). Without Nafion, the response of the sensor toward hydrazine varies by 23.5% after five cycles, while the current change is not noticeable when the sensing area (PEDOT:PSS/ZnO) is covered by Nafion. This suggests that Nafion improves the

long-term mechanical stability against unspecific redox reactions during electrode operation. The first ten CV cycles showing the catalytic response of unmodified PEDOT:PSS/Nafion and ZnO-modified PEDOT:PSS/Nafion electrodes to 5 mM of hydrazine are presented in Figures 1d and 1e, respectively. We observe that ZnO increases the current amplitude in response to hydrazine (the current of the unmodified electrode is lower [i.e., 23%] than that of PEDOT:PSS/ZnO/Nafion film), but it also significantly improves the stability of unmodified PEDOT:PSS/Nafion film. We postulate that the attractive electrostatic interactions between positively charged ZnO and negatively charged Nafion create affinity, thus providing good stability.

Please insert Fig. 2. here

The cross-section SEM images of printed PEDOT:PSS layers and PEDOT:PSS/ZnO/Nafion layers are shown in Figures 2a and 2b, respectively. Ten layers each of PEDOT:PSS, ZnO, and Nafion were printed onto glass to improve visualization (Figure 2b). The thicknesses were 700 nm for ten layers of PEDOT:PSS and 600 nm for a combination of ten layers of ZnO and ten layers of Nafion, approximately. The XRD spectrum in Figure 2c indicates that a ZnO sol-gel modified PEDOT-PSS electrode has peaks representing crystallinity. The strongest diffraction peaks observed at 24.74, 29.03, 37.28, 38.68, 47.21, 54.64, 62.21, and 69.79 belong to the lattice planes (100), (002), (101), (102), (110), (103), (112), and (201). ZnO exists in three crystal lattice structures, i.e. wurtzite (B4), zinc blende (B3), and rock salt (B1) [29]. The lattice planes found in our spectra correspond to the hexagonal wurtzite structure of ZnO. However, no diffraction peak can be observed for the pure PEDOT:PSS film. Although minor additional peaks related to impurities were noticed in the XRD spectra, the sharpness and strong intensity of ZnO diffraction peaks indicate that the synthesized ZnO sample has a crystalline structure [27]. The effect of inkjet printing a ZnO sol-gel layer on top of the PEDOT:PSS surface on the morphology of the working electrode was analyzed based on the topographical AFM images, as shown in Figures 2d and 2e. The surface roughness of PEDOT:PSS film was increased from 0.14 to 0.20 μm after modification with ZnO sol-gel (Figure S3). The

confirmation of the increase in surface area of the working electrode after the ZnO treatment is supported by topographical AFM images. Therefore, we assumed that ZnO sol-gel modification contributed to the enhanced electrocatalytic activity of the sensor.

Please insert Fig. 3. here

3.2. Amperometric detection of hydrazine

The sensitivity of PEDOT:PSS/Nafion and PEDOT:PSS/ZnO/Nafion sensors toward hydrazine (10 μM – 2 mM) was measured by chronoamperometry at 0.5 V (Figures 3a, b). Cyclic Voltammograms (CVs) evidenced that the oxidation process began around +0.4 V and the anodic peak increased until +0.6V, therefore the applied potential values of +0.4, +0.5 and +0.6V were investigated. Hydrazine detection using PEDOT:PSS/Nafion sensor was limited when +0.6V is applied as the printed electrodes were over oxidized, evidenced by color change of the sensing area, leading to a high signal instability. Besides, PEDOT:PSS/ZnO/Nafion sensors response reached a threshold limit value after successive additions of high hydrazine concentrations due to the saturation of the reaction, for instance after measuring first four concentrations (20, 40, 60, 80 μM) of hydrazine (Figure S4a). At +0.4V, sensitivity towards hydrazine additions and stability and sensitivity of signals were undetectable and insignificant (Figure S4c). We concluded that the applied potential of +0.4V did not represent the oxidation happening onto our electrode surface. Hence, the applied potential was selected as +0.5V for the amperometric measurement of the sensor upon the successive additions of hydrazine. The sensor exhibited a rapid and sensitive response to the change of hydrazine concentration, and an obvious increase in the oxidation current upon successive additions of hydrazine. During the calibration measurements and before any injection, we waited for 400 seconds for PEDOT:PSS/Nafion and 500 seconds for PEDOT:PSS/ZnO/Nafion sensor to ensure that the baseline current (in PBS, no hydrazine) was stabilized before the addition of hydrazine. The stabilization of the pre-injection signal and the response time of the signal is higher for

PEDOT:PSS/ZnO/Nafion sensor. This stabilization is considered as blank. As shown in Figures 3c and 3d, the linear range of both sensors is confined to 10 to 500 μM of hydrazine. Further increase of hydrazine concentrations leads to a saturation of the current response. The sensitivity of the sensors at this range was calculated from the slope of calibration curves (inset of Figures 3c and d) and the surface area of the working electrode. The hydrazine sensitivity of the printed PEDOT:PSS/Nafion device is $0.07 \mu\text{A} \cdot \mu\text{M}^{-1} \cdot \text{cm}^{-2}$. The limit of detection of this device is 20 μM based on a signal and noise ratio of 3. The sensitivity and detection limit of the PEDOT:PSS/ZnO/Nafion device is much higher, i.e., $0.14 \mu\text{A} \cdot \mu\text{M}^{-1} \cdot \text{cm}^{-2}$ and 5 μM , respectively. This comparison reveals that ZnO particles enhance the electrocatalytic activity on the sensing area and lead to an increase in the current response and, hence, sensitivity. Our fully printed sensor (PEDOT:PSS/ZnO/Nafion) has higher sensitivity and a lower limit of detection than many reports summarized in Table 1. [28-41] In addition, our paper-based analytical device has advantages of low cost and light weight. Paper-based systems are promising in that they require minimal instrumentation and biocompatibility. These paper-based tools are useful for POC applications and affordable for extending remote sensing applications. Besides, inkjet-printing technology is a more precise electrode-deposition technique than drop casting, which has been reported many times in the production of electrochemical sensors (Table 1).

Please insert Fig. 4. here

Additionally, we investigated the electrochemical interface behavior of electrode and solution by measuring CV responses of the sensors at different scan rates (25–250 mV/s) in the absence of hydrazine (Figure S5) and the presence of 0.5 mM of hydrazine (Figures 4a, c for PEDOT:PSS/Nafion and Figures 4b, d for PEDOT:PSS/ZnO/Nafion). For both sensors, the oxidation current increases with an increase in scan rate. The electrocatalytic current of hydrazine linearly scales with the square root of the scan rate in the indicated range, verifying that the diffusion of hydrazine controls the kinetics of the overall sensor response [42]. Moreover, the plots once more show that the

PEDOT:PSS/ZnO/Nafion sensor has higher linearity ($R^2=0.998$) than the PEDOT:PSS/Nafion sensor ($R^2=0.922$).

3.3. Selectivity, reproducibility and storage tests

The selectivity of the sensors was evaluated by measuring the CV responses to different interfering species (i.e., K^+ , Cl^- , Na^+ , Cu^{2+} , SO_4^{2-} , NO_3^- , methylhydrazine, and phenylhydrazine) added into 0.1 M of PBS solution containing 5 mM of hydrazine. In Figure 5a, we observe that the current response of the PEDOT:PSS/Nafion sensor varies in the presence of interference species, while this change is very limited if ZnO is printed on top of the PEDOT:PSS (Figure 5b), evidencing the improved selectivity of the ZnO-modified PEDOT:PSS layer for hydrazine. Our assumption is that the electrochemical reaction of hydrazine coming from the presence of ZnO onto the PEDOT:PSS electrode causes a change in the current flowing between the working and counter electrodes, proportional to the concentration of hydrazine. ZnO reveals the surface with positive charges since the zeta potential of ZnO is +18 mV (pH 7.0) [43]. As a result, even if Nafion allows them to pass, ZnO exerts repulsive forces toward positively charged species [44]. By contrast, Nafion, a permselective negatively charged membrane, repels anionic species, helping to block negatively charged interferences. At a pH value lower than pKa value of hydrazine (pKa 7.9), hydrazine will be present in its protonated form. This form of hydrazine tends to have a repulsion from the electrode surface. This behavior leads to an increase in overpotential and decrease in peak current values. However, when the pH of the solution is close to the pKa value of hydrazine, hydrazine remains in its neutral form, promoting its facile diffusion through Nafion and interaction with ZnO. To achieve the best possible interaction between positively and negatively charged species and current response, we therefore worked with PBS at pH 7.4, which is a value close to pKa of hydrazine [45].

Please insert Table 1. here

Next, we evaluated the reproducibility of the printed sensors by measuring ten cycles of CV responses of five different devices in 0.1 M PBS in the presence of 5 mM of hydrazine (Figures 5c,

d). The device-to-device reproducibility is about 92% and 70%, respectively, for PEDOT:PSS/ZnO/Nafion and PEDOT:PSS/Nafion sensors. Moreover, we compared the shelf life of the printed sensors. The electrodes were stored at room temperature, and their responses were measured after five, fifteen, and thirty days. After one month of storage, the sensing performance of the ZnO-modified device showed 3% of current loss, while the current response of the unmodified device reduced to 15% of its initial current at day one, confirming the superior stability of the PEDOT:PSS/ZnO/Nafion device (Figure S6). Overall, we postulate that the presence of ZnO nanoparticles enhances the stability, selectivity, reproducibility, and shelf life of the inkjet-printed PEDOT:PSS/Nafion sensor toward hydrazine detection.

Please insert Fig. 5. Here

3.4. Real sample analysis

Two concentrations of hydrazine, 40 μM and 100 μM , were used to spike five water samples from different sources and were analyzed under optimized conditions by using ZnO sol-gel modified PEDOT:PSS/Nafion sensors. The amperometric change of PEDOT:PSS/ZnO/Nafion sensors in each water sample was monitored in three successive chronoamperometry measurements. The hydrazine concentrations measured by our sensor and the recovery percentage results are shown in Table 2. The recovery values are in the range of 88.7 to 97.7% for 40 μM and 98.7 to 104.2% for 100 μM of hydrazine-spiked water samples. The appreciable recoveries add additional evidence to the selectivity and reliability of our paper sensors. Indeed, real samples collected from water bodies are known to contain several kinds of metal ions and salts. ANOVA test (95% confidence interval) was applied to verify whether there is a difference between the results obtained in the detection of hydrazine in real samples. The results showed that there is no statistical difference in obtained hydrazine concentration values from different real samples. Our results are satisfactory and match the recovery values of hydrazine sensors previously reported in the literature [46, 47], evidencing that the proposed printed sensor is a good candidate for the determination of hydrazine in real water samples.

Please insert Table 2. Here

4. Conclusion

We demonstrated a technologically convenient and rapid method for electrode fabrication from pre-synthesized PEDOT:PSS and ZnO sol-gel materials. PEDOT:PSS/Nafion and PEDOT:PSS/ZnO/Nafion sensors were obtained by inkjet printing. Nafion was used for encapsulation for both sensors. The proposed sensor is the first report of a fully inkjet-printed hydrazine sensor fabricated on a disposable, flexible, recyclable paper substrate, which detects hydrazine with a shelf life of one month. The performance of fabricated sensors for the detection of hydrazine was evaluated using chronoamperometry and cyclic voltammetry. Our results showed that the oxidation of hydrazine is catalyzed by ZnO particles. After the modification of the PEDOT:PSS working area with ZnO sol-gel, the sensor sensitivity and stability toward hydrazine were significantly improved (50% and 23%, respectively). It was shown that the PEDOT:PSS/ZnO/Nafion device (sensitivity of $0.14 \mu\text{A}\mu\text{M}^{-1}\text{cm}^{-2}$) is more sensitive to amperometric determination of hydrazine than the PEDOT:PSS/Nafion device (sensitivity of $0.07 \mu\text{A}\mu\text{M}^{-1}\text{cm}^{-2}$) in the range of 10 to 500 μM . Printing one layer of Nafion on top of the working area enhanced the long-term mechanical stability. This work provides evidence that fully inkjet-printed PEDOT:PSS/ZnO/Nafion paper-based sensors have good applicability for the detection of hydrazine in different and complex sample matrices, such as seawater, in a wide range of concentrations and with high stability. We believe that PEDOT:PSS based and fully inkjet printed device concept is a stepping-stone of the next generation disposable,

wearable, user friendly, cost effective and biocompatible paper based electrochemical sensors for not only the detection of hydrazine, but also for the detection of various other dangerous chemicals.

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests

Acknowledgments

The authors would like to acknowledge the financial support of funding from King Abdullah University of Science and Technology (KAUST), Saudi Arabia.

References

- [1] R.F. Kimball, Mutagenicity of Hydrazine and Some of Its Derivatives, *Mutation Research*, 39(1977) 111-26.
- [2] R. Devasenathipathy, S. Palanisamy, S.M. Chen, C. Karuppiyah, V. Mani, S.K. Ramaraj, et al., An Amperometric Biological Toxic Hydrazine Sensor Based on Multiwalled Carbon Nanotubes and Iron Tetrasulfonated Phthalocyanine Composite Modified Electrode, *Electroanal*, 27(2015) 1403-10.
- [3] M.O. Tirunarayanan, W.A. Vischer, Effect of Vitamins on the Acute Toxicity of Hydrazine Derivatives, *Experientia*, 12(1956) 291-2.
- [4] K.C. Back, A.A. Thomas, Aerospace Problems in Pharmacology and Toxicology, *Annual Review of Pharmacology*, 10(1970) 395-&.
- [5] S. Garrod, M.E. Bollard, A.W. Nichollst, S.C. Connor, J. Connelly, J.K. Nicholson, et al., Integrated metabonomic analysis of the multiorgan effects of hydrazine toxicity in the rat, *Chemical Research in Toxicology*, 18(2005) 115-22.
- [6] C. Batchelor-McAuley, C.E. Banks, A.O. Simm, T.G.J. Jones, R.G. Compton, The electroanalytical detection of hydrazine: A comparison of the use of palladium nanoparticles supported on boron-doped diamond and palladium plated BDD microdisc array, *Analyst*, 131(2006) 106-10.
- [7] D.P. Elder, D. Snodin, A. Teasdale, Control and analysis of hydrazine, hydrazides and hydrazones-Genotoxic impurities in active pharmaceutical ingredients (APIs) and drug products, *Journal of Pharmaceutical and Biomedical Analysis*, 54(2011) 900-10.
- [8] W.H. Guo, J.G. Ma, X.H. Cao, X.L. Tong, F. Liu, Y.H. Liu, et al., Amperometric sensing of hydrazine using a magnetic glassy carbon electrode modified with a ternary composite prepared from Prussian blue, Fe₃O₄ nanoparticles, and reduced graphene oxide, *Microchimica Acta*, 184(2017) 3163-70.
- [9] S.R. Hosseini, S. Ghasemi, M. Kamali-Rousta, Preparation of CuO/NiO composite nanofibers by electrospinning and their application for electro-catalytic oxidation of hydrazine, *Journal of Power Sources*, 343(2017) 467-76.

- [10] H. Karimi-Maleh, M. Moazampour, A.A. Ensafi, S. Mallakpour, M. Hatami, An electrochemical nanocomposite modified carbon paste electrode as a sensor for simultaneous determination of hydrazine and phenol in water and wastewater samples, *Environmental Science and Pollution Research*, 21(2014) 5879-88.
- [11] M. Georgea, K.S. Nagarajaa, N. Balasubramanian, Spectrophotometric determination of hydrazine, *Talanta*, 75(2008) 27-31.
- [12] Q.S. Zhai, W.Y. Feng, G.Q. Feng, Rapid detection of hydrazine in almost wholly water solution and in living cells with a new colorimetric and fluorescent turn-on probe, *Analytical Methods*, 8(2016) 5832-7.
- [13] R. Ahmad, T. Beduk, S.M. Majhi, K.N. Salama, One-step synthesis and decoration of nickel oxide nanosheets with gold nanoparticles by reduction method for hydrazine sensing application, *Sensors and Actuators B-Chemical*, 286(2019) 139-47.
- [14] R. Ahmad, O.S. Wolfbeis, Y.B. Hahn, H.N. Alshareef, L. Torsi, K.N. Salama, Deposition of nanomaterials: A crucial step in biosensor fabrication, *Materials Today Communications*, 17(2018) 289-321.
- [15] B. Fang, C.H. Zhang, W. Zhang, G.F. Wang, A novel hydrazine electrochemical sensor based on a carbon nanotube-wired ZnO nanoflower-modified electrode, *Electrochimica Acta*, 55(2009) 178-82.
- [16] S. Kumar, G. Bhanjana, N. Dilbaghi, A. Umar, Zinc oxide nanocones as potential scaffold for the fabrication of ultra-high sensitive hydrazine chemical sensor, *Ceramics International*, 41(2015) 3101-8.
- [17] J.M. Deng, S.J. Deng, Y.B. Liu, Highly Sensitive Electrochemical Sensing Platform for Hydrazine Detection, *International Journal of Electrochemical Science*, 13(2018) 3566-74.
- [18] J. Hu, Z.T. Zhao, Y.J. Sun, Y. Wang, P.W. Li, W.D. Zhang, et al., Controllable synthesis of branched hierarchical ZnO nanorod arrays for highly sensitive hydrazine detection, *Applied Surface Science*, 364(2016) 434-41.
- [19] J.W. Ding, S.Y. Zhu, T. Zhu, W. Sun, Q. Li, G. Wei, et al., Hydrothermal synthesis of zinc oxide-reduced graphene oxide nanocomposites for an electrochemical hydrazine sensor, *Rsc Advances*, 5(2015) 22935-42.

- [20] S. Inal, J. Rivnay, A.O. Suiu, G.G. Malliaras, I. McCulloch, Conjugated Polymers in Bioelectronics, *Accounts of Chemical Research*, 51(2018) 1368-76.
- [21] S. Sakkopoulos, E. Vitoratos, Differentiation of the Aging Process of PEDOT:PSS Films under Inert Helium and Ambient Atmosphere for Two Different Rates of Thermal Treatment, *Open Journal of Organic Polymer Materials*, Vol.04No.01(2014) 5.
- [22] D. Nilsson, T. Kugler, P.O. Svensson, M. Berggren, An all-organic sensor-transistor based on a novel electrochemical transducer concept printed electrochemical sensors on paper, *Sensors and Actuators B-Chemical*, 86(2002) 193-7.
- [23] E.G. Tolstopjatova, V.V. Kondratiev, S.N. Eliseeva, Multi-layer PEDOT:PSS/Pd composite electrodes for hydrazine oxidation, *Journal of Solid State Electrochemistry*, 19(2015) 2951-9.
- [24] E. Bihar, T. Roberts, M. Saadaoui, T. Herve, J.B. De Graaf, G.G. Malliaras, Inkjet-Printed PEDOT:PSS Electrodes on Paper for Electrocardiography, *Advanced Healthcare Materials*, 6(2017).
- [25] E. Bihar, S. Wustoni, A.M. Pappa, K.N. Salama, D. Baran, S. Inal, A fully inkjet-printed disposable glucose sensor on paper, *npj Flexible Electronics*, 2(2018) 30.
- [26] M.M. Rahman, H.B. Balkhoyor, A.M. Asiri, Ultrasensitive and selective hydrazine sensor development based on Sn/ZnO nanoparticles, *Rsc Advances*, 6(2016) 29342-52.
- [27] M.F. Khan, A.H. Ansari, M. Hameedullah, E. Ahmad, F.M. Husain, Q. Zia, et al., Sol-gel synthesis of thorn-like ZnO nanoparticles endorsing mechanical stirring effect and their antimicrobial activities: Potential role as nano-antibiotics, *Scientific Reports*, 6(2016).
- [28] Y.H. Ni, J.S. Zhu, L. Zhang, J.M. Hong, Hierarchical ZnO micro/nanoarchitectures: hydrothermal preparation, characterization and application in the detection of hydrazine, *Crystengcomm*, 12(2010) 2213-8.
- [29] A. Umar, M.S. Akhtar, A. Al-Hajry, M.S. Al-Assiri, G.N. Dar, M.S. Islam, Enhanced photocatalytic degradation of harmful dye and phenyl hydrazine chemical sensing using ZnO nanourchins, *Chemical Engineering Journal*, 262(2015) 588-96.
- [30] M. Wu, W. Ding, J.L. Meng, H.M. Ni, Y. Li, Q.H. Ma, Electrocatalytic Behavior of Hemoglobin Oxidation of Hydrazine Based on ZnO Nano-rods with Carbon Nanofiber Modified Electrode, *Analytical Sciences*, 31(2015) 1027-33.

- [31] C. Wang, L. Zhang, Z.H. Guo, J.G. Xu, H.Y. Wang, K.F. Zhai, et al., A novel hydrazine electrochemical sensor based on the high specific surface area graphene, *Microchimica Acta*, 169(2010) 1-6.
- [32] S. Ameen, M.S. Akhtar, H.S. Shin, Hydrazine chemical sensing by modified electrode based on in situ electrochemically synthesized polyaniline/graphene composite thin film, *Sensors and Actuators B-Chemical*, 173(2012) 177-83.
- [33] T. Rebis, M. Sobkowiak, G. Milczarek, Electrocatalytic oxidation and detection of hydrazine at conducting polymer/lignosulfonate composite modified electrodes, *Journal of Electroanalytical Chemistry*, 780(2016) 257-63.
- [34] M.R. Majidi, A. Jouyban, K. Asadpour-Zeynali, Electrocatalytic oxidation of hydrazine at overoxidized polypyrrole film modified glassy carbon electrode, *Electrochimica Acta*, 52(2007) 6248-53.
- [35] A. Maleki, R. Rezaee, H. Daraei, B. Shahmoradi, N. Amini, Fabrication of a sensitive electrochemical sensor to environmental pollutant of hydrazine in real water samples based on synergistic catalysis of Ag@C core-shell and polyalizarin yellow R, *Journal of Alloys and Compounds*, 763(2018) 997-1004.
- [36] A. Umar, M.M. Rahman, Y.B. Hahn, ZnO Nanorods Based Hydrazine Sensors, *Journal of Nanoscience and Nanotechnology*, 9(2009) 4686-91.
- [37] J.P. Liu, Y.Y. Li, J.A. Jiang, X.T. Huang, C@ZnO nanorod array-based hydrazine electrochemical sensor with improved sensitivity and stability, *Dalton Transactions*, 39(2010) 8693-7.
- [38] J.P. Metters, F. Tan, R.O. Kadara, C.E. Banks, Platinum screen printed electrodes for the electroanalytical sensing of hydrazine and hydrogen peroxide, *Analytical Methods*, 4(2012) 1272-7.
- [39] H.Y. Sun, S.G. Zhao, F.L. Qu, Gold nanoparticles modified ceria nanoparticles for the oxidation of hydrazine with disposable screen-printed electrode, *Measurement*, 45(2012) 1111-3.
- [40] J. Panchompoo, L. Aldous, C. Downing, A. Crossley, R.G. Compton, Facile Synthesis of Pd Nanoparticle Modified Carbon Black for Electroanalysis: Application to the Detection of Hydrazine, *Electroanal*, 23(2011) 1568-78.

- [41] J. Zhang, J.K. Xu, Y.P. Wen, Z.F. Wang, H. Zhang, W.C. Ding, Voltammetric determination of phytoinhibitor maleic hydrazide using PEDOT:PSS composite electrode, *Journal of Electroanalytical Chemistry*, 751(2015) 65-74.
- [42] J.W. Wu, T.T. Zhou, Q. Wang, A. Umar, Morphology and chemical composition dependent synthesis and electrochemical properties of MnO₂-based nanostructures for efficient hydrazine detection, *Sensors and Actuators B-Chemical*, 224(2016) 878-84.
- [43] K.Y. Hwa, B. Subramani, Synthesis of zinc oxide nanoparticles on graphene-carbon nanotube hybrid for glucose biosensor applications, *Biosensors & Bioelectronics*, 62(2014) 127-33.
- [44] F.M. Omar, H.A. Aziz, S. Stoll, Aggregation and disaggregation of ZnO nanoparticles: Influence of pH and adsorption of Suwannee River humic acid, *Science of the Total Environment*, 468(2014) 195-201.
- [45] R. Madhu, B. Dinesh, S.M. Chen, R. Saraswathi, V. Mani, An electrochemical synthesis strategy for composite based ZnO microspheres-Au nanoparticles on reduced graphene oxide for the sensitive detection of hydrazine in water samples, *Rsc Advances*, 5(2015) 54379-86.
- [46] H.M.A. Amin, M.F. El-Kady, N.F. Atta, A. Galal, Gold Nanoparticles Decorated Graphene as a High Performance Sensor for Determination of Trace Hydrazine Levels in Water, *Electroanal*, 30(2018) 1749-58.
- [47] I.M. Isa, S. Saruddin, N. Hashim, M. Ahmad, S. Ab Ghani, Determination of Hydrazine in Various Water Samples by Square Wave Voltammetry with Zinc-Layered Hydroxide-3(4-methoxyphenyl) Propionate Nanocomposite Modified Glassy Carbon Electrode, *International Journal of Electrochemical Science*, 11(2016) 4619-31.

Tutku Bedük received her bachelor degree from Middle East Technical University in Chemistry with a High Honor Degree, Turkey in 2016. She also completed her MSc degree in Bilkent University in the field of Chemistry, Turkey in 2018. She is currently a PhD candidate in the Sensor Lab Group under the direction of Prof. Khaled Nabil Salama at King Abdullah University of Science in Saudi Arabia. Her professional interests focus on developing enzymatic and non-enzymatic biological and chemical sensing platforms.

Eloise Bihar received her MSc degree from Grenoble INP-Pagora, Grenoble(France) in 2010 and her Ph.D degree from Microelectronics, école des Mines de Saint Etienne, Gardanne, France, in 2016. She is currently working as a Postdoctoral Research Fellow at King Abdullah University of Science and Technology (KAUST), Kingdom of Saudi Arabia. Bihar's current research focuses on the fabrication of printed autonomous biosensors for monitoring human metabolites. She aims to develop cutaneous, minimally invasive and conformable sensors mounted on the skin. She has published her recent research in highly impacted journals.

Sandeep G Surya is currently working as a Postdoctoral Research Fellow at King Abdullah University of Science and Technology (KAUST), Kingdom of Saudi Arabia. He received Ph.D degree from CRNTS, IIT Bombay and B.Tech. degree from JNTU, Hyderabad. He worked as Research Associate at Microsystems Technology Research Unit, CMM, Fondazione Bruno Kessler (FBK), Trento, Italy. He is member of a group working on developing a stand-off explosive detection technology using OFETs and nano-electro-mechanical-sensors. He was also a member of the team e-sanjeevani, which developed a project on Telemedicine which earned wide recognition and was adjudged 1st in many national level symposia. His work won GANDHIAN YOUNG TECHNOLOGICAL INNOVATION AWARD at IIM-A 2012, the Fellowship at ISED 2011, the best novelty prize for humanoid robot at IIIT-H and the P.P CHHABRIA AWARD OF EXCELLENCE in intelligent systems and robotics for the year 2009 at IIIT, Pune.

Aminta Naidili Castillo Robles received her bachelor's degree in Electrical Engineering in the University of Arkansas, United States in 2015. As an undergraduate, she worked as a researcher designing the first RS-485 with a SiC technology. She became a research assistant obtaining her M.Sc. in Electrical Engineering at the University of Arkansas, United States in 2015. While studying her masters she designed a Silicon Germanium CMOS Linear Voltage Regulator for Agricultural Applications. She completed her internship in Electrical Engineering Department of King Abdullah University of Science and Technology Her professional interests are computer-aided for mixed-signal integrated circuit design, process/device development, and biosensing.

Sahika Inal is an Assistant Professor in the Biological and Environmental Science and Engineering department at King Abdulllah University of Science and Technology. She received her PhD in Experimental Physics, University of Potsdam (UP), Germany, 2013. Professor Inal designs electronic devices that can efficiently communicate with biological systems. Her research interests cover organic electronic materials and devices that can address research and clinical health monitoring and therapy needs. She is particularly interested in ionic-electronic conduction in organic electronic materials and explores the potential of these materials for recording biological signals and modulating biological events. While investigating transport in organic electronics, she functionalizes these materials to make seamless interfaces with human body.

Khaled Nabil Salama is a Professor and founding chair member in the Electrical engineering department at King Abdulllah University of Science and Technology. He received his PhD in electrical engineering from Stanford University in 2005. He is a prominent researcher in the field of memristor-based devices. He is currently working on applications of modern electrical analog circuits. He has been active and highly successful in bringing multiple inter-disciplinary fields in biology, microwave engineering, chemistry, material sciences, and mechanical engineering with electrical engineering. He works on application of modern devices to build biomedical sensors. Professor Salama publishes regularly in IEEE Transactions. He is the 4th highest cited author in the area of memristors.

He has 15 patents (9 at KAUST) in his name and has founded two startups. He had served as Associate Editor on two premier journals, the IEEE Transactions on Circuits and Systems and the IEEE Transactions on Biomedical Circuits and Systems. He also served as a technical program committee member on leading conferences such as IEEE VLSI, IEEE Sensors and IEEE ISCAS. Professor Salama is a senior member of the IEEE.

Figures

Figure 1: (a) Schematic of sensor comprising working, reference and counter electrode with as printed PEDOT:PSS layer, insulator, ZnO sol-gel and the encapsulation layer (Nafion). (b) Photograph of the fully printed flexible sensor. CV response of (c) PEDOT:PSS/ ZnO sol-gel/Nafion at 0 (Bare), 0.1, 0.5, 1, 5 mM of hydrazine in 0.1 M PBS (pH 7.4). Stability test of sensors made of (d) PEDOT:PSS/Nafion and (e) ZnO sol-gel modified PEDOT:PSS/Nafion after 10 cycles in 5 mM hydrazine. Scan speed: 50 mV/s.

Figure 2: Cross-section FE-SEM images of inkjet-printed (a) PEDOT:PSS film (ten layers), (b) PEDOT:PSS/ZnO/Nafion (ten layers), (c) XRD data of PEDOT:PSS/ZnO (red), PEDOT:PSS working electrode surface (black). Atomic force microscope (AFM) images of (d) PEDOT:PSS/ZnO and (e) PEDOT:PSS electrode surface.

Figure 3: Current-time characteristics of printed (a) PEDOT:PSS/Nafion sensor, (b) PEDOT:PSS/ZnO/Nafion sensor in response to different concentrations of hydrazine added successively into 0.1 M PBS (pH 7.4). The applied voltage is 0.5 V vs PEDOT:PSS reference electrode printed on the sensor. The change in the oxidation current is a function of hydrazine concentrations for (c) PEDOT:PSS/Nafion sensor, (d) PEDOT:PSS/ZnO/Nafion. The inset is the calibration curve of the range for low hydrazine concentrations.

Figure 4: Cyclic voltammetry curves of inkjet-printed (a) PEDOT:PSS/Nafion, (b) PEDOT:PSS/ZnO/Nafion sensor in 0.1 M PBS (pH 7.4) containing 0.5 mM of hydrazine acquired at scan rates varying from 25 to 250 mV/s. (c–d) Peak current vs the square root of scan rate (v). The peak currents are extracted from a) and b) and are linearly proportional with the square root of scan rate.

Figure 5: The bar chart shows the current response of the sensor to 5 mM of hydrazine coexisting in the solution with 5 mM of each interfering species (i.e., K^+ , Cl^- , Na^+ , Cu^{2+} , SO_4^{2-} , NO_3^- , methylhydrazine, and phenylhydrazine). (a) PEDOT:PSS/Nafion and (b) ZnO sol-gel modified PEDOT:PSS/Nafion. The scan rate is 50 mV/s. Reproducibility test of five different sensors (c) PEDOT:PSS/Nafion and (d) ZnO sol-gel modified PEDOT:PSS/Nafion sensors in 5 mM hydrazine in 0.1M PBS (pH 7.4) at 50 mV/s.

Fig. 1.

Fig. 2. **Fig. 3.**

Fig. 4.

Fig. 5.

Tables

Table 1. Comparisons of Zinc Oxide and polymer based hydrazine sensor performance with our sensor.

Modified Electrode	Fabrication Method	Detection method	Sensitivity ($\mu\text{A}\mu\text{M}^{-1}\text{cm}^{-2}$)	Linear range (μM)	LOD (μM)	Ref.
Flower-like ZnO	Drop casting	Amperometric	0.095	-	2.1	[28]
ZnO NUs/BCA/GCE	Drop casting	LSV	0.0421	98-3.126	78.6	[29]
Hb/ZnO/CNF/GCE	Drop casting	Amperometric	0.0147	19.8–1710	6.6	[30]
PSS/Graphene/GCE	Drop casting	Amperometric	-	3-300	1	[31]
PANI/Gr/FTO	Electropolymerization	Amperometric	0.325	10,000-100,000	15380	[32]
GCE/PEDOT/LS	Electropolymerization	Amperometric	-	15–290	9.8	[33]
GCE/PPy/LS	Electropolymerization	Amperometric	-	2.0–75	1.65	[33]
Polypyrrole/GCE	Electropolymerization	Amperometric	0.482	1.3–2000	3.6	[34]
PAYR/Ag@C	Electropolymerization	Amperometric	0.0666	1-1320	0.25	[35]
ZnO NRs.Au	Direct Growth	Amperometric	0.0038	3.0–300	2.2	[36]
C@ZnO	Direct growth	Chronoamperometric	0.00476	0.2-2.0	0.1	[37]
PtSPE	Screen Printing	Voltammetric	-	50-500	0.12	[38]
AuNP-CeO ₂ /Graphite-ink	Screen Printing	Voltammetric	-	10-10000	-	[39]
Pd/CB	Drop Casting	Chronoamperometric	-	5-500	8.8	[40]
PEDOT:PSS-CMC-SWCNT/GCE	Drop Casting	Voltammetric	-	10-100 0.8-51	0.1 0.1	[41]
ZnO NPs/PEDOT:PSS	Inkjet printing	Chronoamperometric	0.14	10-500	5	This Work

Abbreviations: ZnO-Zinc oxide; GCE- glassy carbon electrode; Hb-hemoglobin; CNF-carbon nanofiber; PSS- poly(styrene sulfonate); PANI-polyaniline; Gr- graphene; FTO- fluorine doped tin oxide; LS- Lignosulfonate; PAYR- poly (alizarin yellow R); Ag- silver; C-carbon; Au- gold; Pt- platinum; SPE-screen printed electrode; CuO- Cuppor oxide; MWCNT-multiwalled carbon nanotubes; Pd- palladium; GCE-glassy carbon electrode; CMC-SWCNT- carboxymethyl cellulose-single-walled carbon nanotubes.

Table 2. Analysis of hydrazine in water samples

Sample	Amount added (μM)	Amount found* (μM)	Recovery (%)	RSD
Tap Water	40	39.7	97.7	4.8
	100	102.5	102.5	2.5
Bottled Water 1	40	37.7	90.3	3.3
	100	104.2	104.2	2.1
Bottled Water 2	40	37.9	91.7	6.0
	100	100.5	100.5	3.9
Bottled Water 3	40	37.9	91.7	6.0
	100	99.5	99.5	2.5
Sea Water	40	37.2	88.7	2.1
	100	96.9	98.7	3.9

*Data followed by the same superscript are not significantly different ($p > 0.05$) by ANOVA and Tukey test.