Sensors and Actuators A 269 (2018) 79–90

Contents lists available at ScienceDirect

Sensors and Actuators A: Physical

journal homepage: www.elsevier.com/locate/sna

A temperature-compensated graphene sensor for nitrate monitoring in real-time application

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ARTICLE INFO

Article history:
Received 5 September 2017
Received in revised form 26 October 2017
Accepted 8 November 2017
Available online 10 November 2017

Keywords:
Graphene sensor
Nitrate monitoring
Printed sensor
Temperature compensation
Smart sensing system
Internet of things (IoT)

ABSTRACT

Low-cost nitrate-N sensors and smart sensing systems are necessary to develop a distributed network to monitor the quality of water in real time. This paper presents the fabrication process of carbon printed sensors and the advantage of using a graphene sensor to measure the concentration of nitrate-N in water. The sensor was characterized at different temperatures and with different nitrate-N concentrations in water. Electrochemical Impedance Spectroscopy (EIS) was employed to characterize the developed sensors. The calibration standard with the temperature compensation is also explained. UV-Spectrometry was used to validate all the results and the range of concentrations was 1–70 ppm. The sensing system has WiFi connectivity to transfer the data to a cloud server to monitor the data in real time. The sensor has shown good performance during measurements and the developed sensing system has very good potential to be a part of a distributed sensing network to monitor the data in real time.

1. Introduction

Nitrogen is an important nutrient for nature's nitrogen cycle for the living beings of earth, and comes from one of the nutrient sources named nitrates. Excessive nitrate leaching losses from soil into water cause a threat to aquatic environments and human health [1–3]. They can be found widely in the environment due to their solubility in water. It is well known that the surface water is contaminated in New Zealand by nitrate ions due to excessive agricultural land use and cattle farming which can pose a serious threat to surface water quality [4,5]. An excessive amount of nitrate-N in rivers help to grow periphyton and macrophytes to nuisance level [6]. They reduce the oxygen level in the water, which can hamper the aquatic life of fish. Contaminated nitrate-N water may cause serious illnesses such as birth defects, spontaneous abortions, intrauterine growth restriction and potential cancer risk [7–10]. Further, long-term accumulation of nitrate-N is a potential risk to animal and human health. The blue-baby-syndrome can be caused by drinking of water with elevated nitrate concentrations [11].

Spectrophotometric method is used to determine nitrate-N in water using chemical reagents [12]. The Griess reaction is used for the reduction of nitrate ions [13]. Ion chromatography [14], optical fiber sensors [15,16], planar electrode sensors [17], ion-selective electrodes [18], palladium nanostructures [19] are used to measure nitrate-N ions in water. Most of them are laboratory-based methods and generate a lot of chemical waste, which is harmful to the environment. In situ measurement systems are also reported [20,21] which were related to impedance spectroscopy.

The regional councils or local government of New Zealand monitors water samples from different sampling locations, such as rivers, lakes, and groundwater. The water manager collects those samples at regular intervals, usually once or twice in a month. The laboratory-based methods such as spectrophotometry or ion chromatography were used to measure nitrate-N concentrations. However, it is difficult to measure accurately the effect of leaching nitrate-N into rivers or lakes due to the fluctuation of dynamic water systems all through New Zealand. Therefore, a monthly sampling measurement would be unable to provide the actual nitrate-N profile. Missing information could influence the understanding of the seasonal effects, and in the process, the total nitrate-N estimation would be wrong. This missing information hampers policymakers from taking proper decision.

The last decade has experienced an unprecedented growth in the use of graphene due to its exceptional electrical and mechanical properties [22]. As a result of its distinctive advantages over other conductive materials [23], graphene has become a popular choice to develop the electrodes of a sensor. Two of the major advantages of using graphene for electrodes are its porosity [24] and corrosion-

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https://doi.org/10.1016/j.sna.2017.11.022
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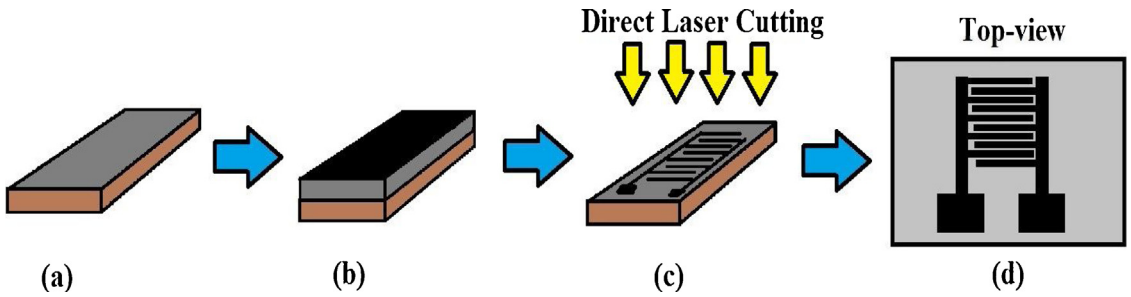

Fig. 1. Schematic diagram of the CNT-PDMS based sensor. (a) PDMS was cast on a PMMA template. (b) A layer of nanocomposite (NC) layer was cast on top of the cured PDMS. (c) The cured NC layer was laser cut to form the electrodes. (d) Final product used as a sensor.

resistant nature [25]. The former characteristic causes an increase in the sensing area of the sensor, whereas the latter prolongs the efficiency of the sensor. The applications of graphene have been in different sectors, primarily in healthcare [26], environmental [27] and industrial [28] areas. This paper showcases the irradiation of a polymer film [29] by a laser sintering technique to generate conductive material. Due to the high electrical conductivity of the graphene film generated by this technique, its use has been largely in micro-supercapacitors [30,31] to reduce the effect of polarization at high frequencies. Less sample preparation time, smooth cuts and perpendicular edges are some of the advantages provided by the laser sintering technique. A minimized number of steps generating porous conductive material with enhanced electrical, mechanical and thermal properties are some of the advantages of the proposed sensor.

This paper explains the fabrication process of Carbon Nanotubes (CNT) – Polydimethylsiloxane (PDMS) and Graphene sensors. Graphene sensors are low cost, which would be useful to measure nitrate-N concentration in water. An Internet of Things (IoT) enabled smart sensing system was also developed to measure the nitrate-N concentration in real time. IoT refers to the internet-connected network objects from everyday life, which is often capable of doing the regular activity cleverly. The purpose of using the IoT is to create an environment in which the basic information of the developed network is shared in real time. The proposed system can also measure the nitrate-N concentration in real time and transfer the data to the cloud server to allow the system to be used as part of a distributed network. A compensation for temperature was also included in the system, which will increase the accuracy of measurement. The fabrication process, nitrate-N and temperature measurement and validation of the smart sensing systems are explained in the subsequent sections.

2. Materials and methods

2.1. Fabrication of the printed sensors

The fabrication of the sensor patches was done at fixed temperature and humidity conditions (temperature: 22 °C, RH: 50%). Fig. 1 shows the schematic diagram of the fabrication steps of the CNT-PDMS based sensor. The Polydimethylsiloxane (PDMS) was cast on a Poly (methyl methacrylate) PMMA template to form the substrate for the sensor patch. PDMS was used to form the sensor patch due to its low-cost, low Young's modulus (E), and hydrophobic nature. PMMA was used due to its non-toxicity and proper adherence with the cured PDMS. Then, a layer of nanocomposite (NC) formed by mixing Multi-Walled Carbon Nanotubes (MWCNTs) and PDMS was cast on the cured PDMS. MWCNTs were considered as the conductive material due to their high electrical conductivity, flexibility, high tensile strength and resistance towards a wide range of temperatures. The curing of the NC layer was followed by the laser cutting of the top layer to form the electrodes of the sensor patch. The individual fabrication steps are shown in Fig. 2. PDMS (SYLGARD ® 184, Silicon Elastomer Base) was formed by mixing a ratio of 10:1 between the base elastomer and curing agent respectively. The height of the PDMS cast on the PMMA was adjusted by a casting knife (SHEEN, 1117/1000 mm) to around 1000 μm. The sample was then desiccated for 2 h to remove any trapped air bubbles. After curing the sample at 80 °C for 8 h, a layer of NC formed by mixing MWCNTs (Aldrich, 773840-100G) and PDMS was cast on top of it. The weight value of the MWCNTs was optimized to have a trade-off between the flexibility of the sensor patch and the conductivity of the electrodes. The final optimized value of the CNTs chosen to form the NC was 4 wt.%. Fig. 3(a) shows a Scanning Electron Microscope (SEM) image of the optimized CNT in the NC. The black regions in the image represent the CNTs while the white spots define the PDMS in the NC. The height of the NC layer was again adjusted by

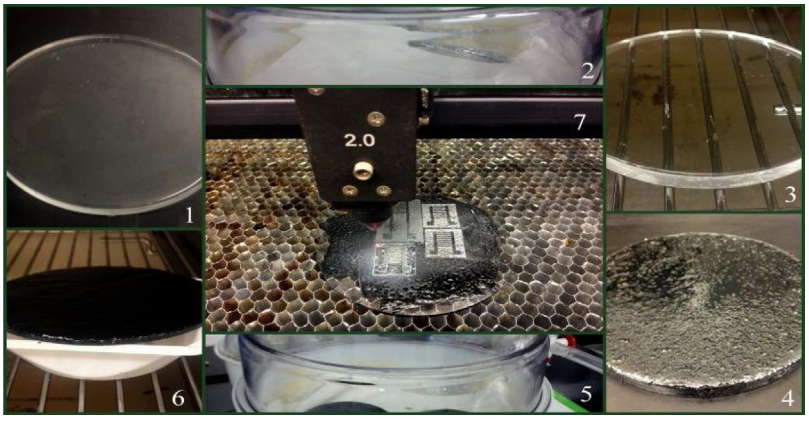

Fig. 2. Individual fabrication steps followed to develop the CNT-PDMS sensor.