



Short communication

Selective detection of F⁻ using Al microarrays integrated graphene oxide

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ABSTRACT

The present study demonstrates, a selective detection of F⁻ using aluminium (Al) micro-interdigitated electrode (μ -IDEs) array modified by graphene oxide (GO). The selectivity of the fabricated sensor towards F⁻ in presence of contaminants like, Chloride (Cl⁻), Bromide (Br⁻) & Nitrate (NO₃⁻) at concentration of 100 and 50 ppm is investigated using simple electrical measurements. The selectivity of GO/Al- μ -IDEs is attributed to the highest electro-negativity and strong affinity of F⁻ towards Al. The real time, cost effective, selective GO/Al- μ -IDEs based molecular sensors shows the potential for detection of aqueous F⁻ in presence of other contaminants.

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1. Introduction

Recently, few reports on the selective detection/removal of aqueous fluoride anions (F⁻) are demonstrated. The selective detection of F⁻ is extremely important as the over exposure of F⁻ leads to several harmful effects [1]. The permissible limit of F⁻ in drinking water as recommended by American Dental Association (ADA), World Health Organization (WHO) and Bureau of Indian Standards (BIS) is around 0.8, 1.5 and 1 ppm, respectively. [1–3]. The traditional approaches for the selective detection of F⁻ includes organic semiconductor [4], silyloxy-functionalized tetraphenylethylene (TPE) derivative [5], tetrathiafulvalene (TTF) [6], ion-chromatography, ion-selective electrodes and spectroscopic techniques [7]. However, the reported techniques lack with real time detection, highly sensitive, low cost, reliability for the selective detection of aqueous F⁻. In addition, few reported techniques make use of complex instruments requiring detection in a specific range of wavelength and also are time consuming, hence difficult to promote globally. The selective detection of F⁻ is also reported by Çiftçi et al. [8], which includes development of electrochemical sensor based on poly(3-aminophenylboronic acid), (PAPBA) modified glassy carbon electrode.

On the other hand, the graphene oxide (GO), based devices have absorbed attention owing to the unique properties and emerged as a potential contender for long-lasting chemical and biological sensors applications [9–11]. Furthermore, besides several advantages of Aluminium (Al) useful as an electrode material as mentioned previously [12], oxidizes to aluminium oxide (Al₂O₃) even at low temperature and is sensitive towards F⁻. Due to the increasing demands for the higher sensitivity and reliability of chemical sensors, micro-interdigitated electrodes (μ -IDEs) are employed extensively [13]. The output signal response using IDE can be controlled through the careful design of the length (*L*), width (*W*), spacing (*D*) and number of μ electrode fingers (*N*) [14]. Therefore, in the present study, μ -IDEs with *W*=*D*= \sim 300 μ m, *N*=17 and *L*= \sim 1 cm is used, top view as shown in Fig. 1(a).

The present work demonstrates a selective detection of F⁻ based on GO/Al- μ -IDEs sensor. The selectivity of the sensor towards F⁻ in presence of contaminants like, halides (Chloride (Cl⁻), Bromide (Br⁻)) and Nitrate (NO₃⁻) is investigated based on simple electrical [Sensing Current–Voltage (*I*–*V*)] measurements using Keithley 4200 Semiconductor Characterization System (SCS). Moreover, the selectivity being the most important characteristics of any sensor. The large surface area of GO boosts the surface loading of anions resulting in improved sensitivity and the formulation of Al₂O₃, which serve as ion exchange centres for the selective sensing of F⁻ in presence of Cl⁻, Br⁻ and NO₃⁻ at concentration of 50 and 100 ppm.

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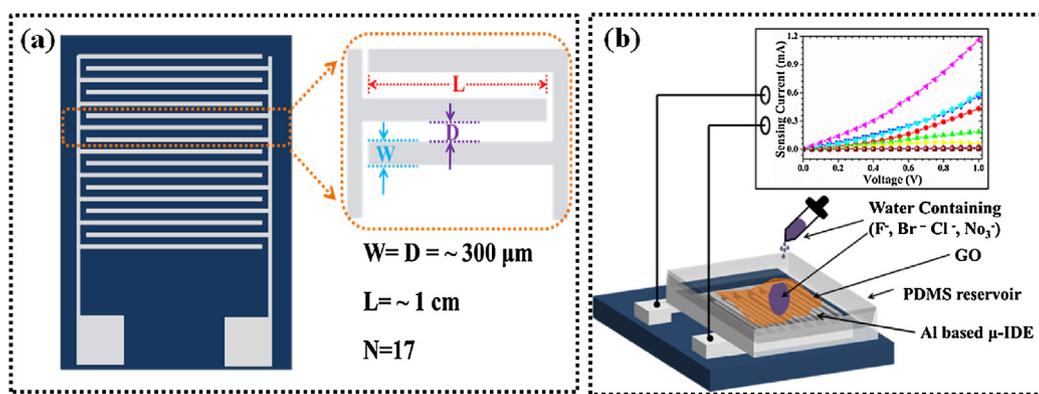


Fig. 1. (a) Top view of Al (μ -IDE)/p-Si sensor array along with its dimensional parameters, (b) setup for measurement of I - V response of the GO/Al- μ -IDEs sensor along with various contaminants.

Table 1

Equivalent PPM and mole concentration of the solutions.

Solution	Concentration in PPM	Concentration in moles (M)
F ⁻	0.1–1000	5.27×10^{-6} – 5.27×10^{-2}
Cl ⁻	50–2000	1.41×10^{-3} – 5.64×10^{-2}
Br ⁻	50–2000	6.26×10^{-4} – 2.5×10^{-2}
NO ₃ ⁻	50–2000	8.06×10^{-4} – 3.23×10^{-2}

2. Materials and methods

2.1. Materials

Analytical grade chemicals were used as received without any purification. Tetrabutylammonium (TBA) salts of fluoride (1 M), Chloride, Bromide (Sigma–Aldrich make) are employed as the source of contaminants due to low cost, ease of solubility in water and non-toxic nature. De-ionized (DI) water (Elga make, UK) with resistivity of 18.2 M Ω -cm is used in the present study. For the selectivity response of the sensor, $\sim 100 \mu\text{l}$ of GO (1 mg/ml) is drop casted over the Al (μ -IDEs)/p-Si, dried (@ 50 °C for 60 min) followed by drop casting nearly 10 μl of the aqueous solution containing different contaminants (F⁻, Cl⁻, Br⁻, NO₃⁻) in the PDMS based reservoir (with dimensions 25 \times 25 \times 8 mm) as shown in Fig. 1(b).

2.2. Stock solution preparation: F⁻, Cl⁻, Br⁻, NO₃⁻

A 10 ml 1000 ppm F⁻ and 2000 ppm Cl⁻, Br⁻ and NO₃⁻ stock solution is prepared by dissolving 0.52 ml, 1 M TBAF and 78.3, 40.3 and 27.4 mg of TBACl, TBABr, NaNO₃ in DI water, respectively. The corresponding equivalent for the concentration of solution in PPM and moles (M) is as shown in Table 1. The further dilutions were performed based on the standard normality equation.

2.3. GO synthesis and fabrication of GO/Al (μ -IDE)/Si sensor

The GO is synthesized based on Modified Hummers method. Our previous report presents the details of GO synthesis and fabrication of Al- μ -IDEs arrays [12,15]. The X-ray diffraction (XRD) (Fig. 2(a)) is carried out for the confirmation of interlayer separation (d-spacing) in GO. The XRD spectra of GO shows a (001) peak at $2\theta = 9.32^\circ$ corresponding to d-spacing $\sim 9.47 \text{ \AA}$ [16,17]. The XPS measurement (C_{1s} spectra) of GO (Fig. 2(b)) de-convoluted into four peaks: C–C/C=C (284.8 eV), C–O (286.3 eV), C=O (287.5 eV) and O–C=O (288.5 eV) [18]. Hence the XPS C_{1s} measurement confirms the available hydrophilic oxygen containing functional groups in GO.

For the selective detection of F⁻ in presence of other contaminants, the electrodes fabricated in the same batch were employed

for the measurement of I - V . But, owing to lack of industrial scale process control, the electrode fabrication results the variation in impedance. Hence, the offset of the samples was adjusted and compensated after the drop cast of GO.

3. Results and discussion

The aqueous F⁻ has high affinity for water molecules and undergoes reversible reaction resulting in a weak acid (HF) along with a strong base (OH⁻). The reaction continues further resulting into hydronium ion (H₃O⁺), F⁻ and so on the process continues [12,19]. Fig. 3(a) shows the I - V characteristic curves for the fabricated GO/Al (μ -IDEs)/p-Si sensor as a function of F⁻ concentration ranging from 0.1 to 10 ppm, from 0 to 1 V. The I - V response of the sensor for GO (reference, without F⁻) increases from 0 to “A” ($\sim 6.95 \mu\text{A}$). The response of the GO/Al (μ -IDEs)/p-Si sensor increases from 0 to “B” ($\sim 66.62 \mu\text{A}$), “C” ($\sim 0.55 \text{ mA}$), “D” ($\sim 0.91 \text{ mA}$) with increase in F⁻ concentration of 0.1, 1 and 10 ppm at 1 V, respectively. The I - V curve for the GO/Al (μ -IDEs)/p-Si sensor shows around 9, 79, 130 times substantial increase in sensing current for F⁻ solution of 0.1, 1 and 10 ppm with respect to GO. Furthermore, for the selectivity investigation of the sensor towards F⁻, the I - V measurement curves in presence of Cl⁻, Br⁻, NO₃⁻ at 50 and 100 ppm (with and without F⁻) is shown in Fig. 3(b). The I - V curves for GO + Br⁻ 100 ppm and GO + NO₃⁻ 100 ppm increases from 0 to “E”, ~ 8.08 and $8.7 \mu\text{A}$, respectively. While in presence of GO + (F⁻ 1 ppm + NO₃⁻ 50 ppm) and GO + (F⁻ 1 ppm + NO₃⁻ 100 ppm), the sensing current increases from 0 to “F” ($\sim 10 \mu\text{A}$) and “G” ($\sim 20.5 \mu\text{A}$), as shown in inset of Fig. 3(b). The sensor response increases from 0 to “H” ($\sim 0.064 \text{ mA}$), “I” ($\sim 0.19 \text{ mA}$), “J” ($\sim 0.42 \text{ mA}$), “C” ($\sim 0.55 \text{ mA}$) and “K” ($\sim 1.15 \text{ mA}$) for GO + Cl⁻ 100 ppm, GO + (F⁻ 1 ppm + Br⁻ 50 ppm), GO + (F⁻ 1 ppm + Br⁻ 100 ppm), GO + (F⁻ 1 ppm + Cl⁻ 50 ppm) and GO + (F⁻ 1 ppm + Cl⁻ 100 ppm), respectively. With the addition of 100 ppm of Br⁻, NO₃⁻, Cl⁻ to GO/Al (μ -IDEs)/p-Si, the sensing current shows a feeble increase of 1.16, 1.25, 9.2 as compared to 1 ppm F⁻ alone (~ 79 times). Additionally, in presence of 1 ppm F⁻, the sensor response for GO + (F⁻ 1 ppm + NO₃⁻ 50 ppm), GO + (F⁻ 1 ppm + NO₃⁻ 100 ppm), GO + (F⁻ 1 ppm + Br⁻ 50 ppm), GO + (F⁻ 1 ppm + Br⁻ 100 ppm), GO + (F⁻ 1 ppm + Cl⁻ 50 ppm) and GO + (F⁻ 1 ppm + Cl⁻ 100 ppm) amplifies to around 1.4, 2.9, 27.3, 60.43, 79 and 165 times, respectively, as summarized in Table 2.

The interaction of the anions (F⁻, Cl⁻, Br⁻, NO₃⁻) with the GO/Al (μ -IDEs)/p-Si sensor is investigated through electrical characterization, shows that there is significant increase in sensing current in presence of F⁻. Owing to the permissible limit of F⁻ (1 ppm, as per ADA, BIS and WHO) in drinking water, in the present study the selectivity of the sensor towards F⁻ is studied by keeping F⁻ concentration at 1 ppm and other anions (Cl⁻, Br⁻, NO₃⁻) as 50

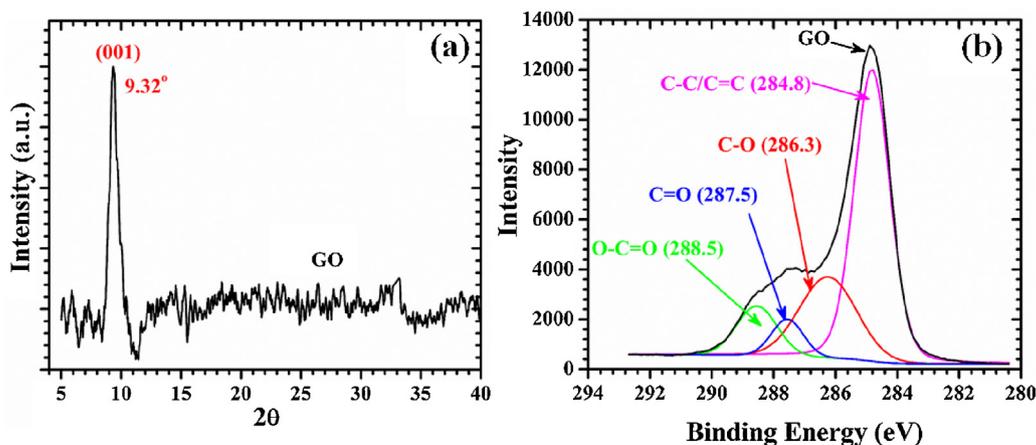


Fig. 2. Shows the (a) XRD, (b) C_{1s} spectra for GO.

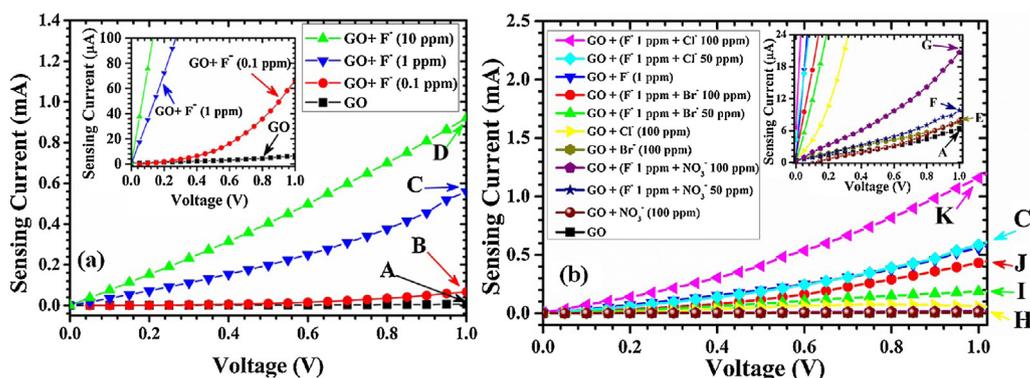


Fig. 3. Sensing current (I)–voltage (V) characteristics for Al (μ -IDEs)/p-Si from 0 to 1 V as a function of (a) GO and GO + F^- (0.1–10 ppm), (b) GO, Cl^- , Br^- , NO_3^- , GO + (F^- , Cl^- , Br^- , NO_3^-), the F^- concentration is fixed at 1 ppm while for Cl^- , Br^- , NO_3^- , is 50 and 100 ppm. Inset shows the zoom in (y -axis) I – V curves.

Table 2

Summary: sensing current and increment with respect to go.

Solution/contamination source	Point as indicated in Fig. 3	Sensing current	Increment w.r.t. GO
GO	A	6.95 μA	–
GO + F^- (0.1 ppm)	B	66.62 μA	9
GO + F^- (1 ppm)	C	0.55 mA	79
GO + F^- (10 ppm)	D	0.91 mA	130
GO + Br^- (100 ppm)	E	8.08 μA	1.16
GO + NO_3^- (100 ppm)	E	8.7 μA	1.25
GO + (F^- 1 ppm + NO_3^- 50 ppm)	F	10 μA	1.4
GO + (F^- 1 ppm + NO_3^- 100 ppm)	G	20.5 μA	2.9
GO + Cl^- (100 ppm)	H	0.064 mA	9.2
GO + (F^- 1 ppm + Br^- 50 ppm)	I	0.19 mA	27.3
GO + (F^- 1 ppm + Br^- 100 ppm)	J	0.42 mA	60.43
GO + (F^- 1 ppm + Cl^- 50 ppm)	C	0.55 mA	79
GO + (F^- 1 ppm + Cl^- 100 ppm)	K	1.15 mA	165

and 100 ppm. The increase in sensing current in presence of F^- is attributed to strong affinity and highest electronegativity of F^- (smallest ion) towards Al and resulted in increased sensing current [12]. The F^- binds with the functional sites available in Al and results in increased sensing current. Similar findings and a detailed mechanism for the reaction between Al and F^- is reported in [12,20].

In presence of F^- (1 ppm) and NO_3^- (50 and 100 ppm), the increase in sensing current is very low (~ 1.4 and 2.9 times, as shown in Table 2) may be due to: (i) lower electronegativity of NO_3^- [21] thus, low affinity towards Al (ii) high concentration of NO_3^- as compared to F^- . Hence, the less reactive NO_3^- (as compared with F^-) [21] tries to bind with the functional sites available in Al and results in saturation in binding sites for F^- . On the other hand, for

Br^- , the GO + (F^- 1 ppm + Br^- 100 ppm) and GO + (F^- 1 ppm + Br^- 50 ppm) the sensing current is lower than that of F^- (1 ppm) but higher as compared with GO + (F^- 1 ppm + NO_3^- 50 ppm), GO + (F^- 1 ppm + NO_3^- 100 ppm) owing to higher electronegativity of Br^- compared with NO_3^- [21]. Similarly, for GO + (F^- 1 ppm + Cl^- 50 ppm), the sensing current is almost equal to current at F^- (1 ppm) and higher than NO_3^- and Br^- (50 and 100 ppm). However, for GO + (F^- 1 ppm + Cl^- 100 ppm), the sensing current increases even higher than F^- (1 ppm). This may be due to high concentration and high affinity (lower than F^-) of Al for Cl^- . The sensing range of the fabricated sensor for F^- (5.27×10^{-6} – 5.27×10^{-4} M) in the present work is comparable with previously reported PAPBA modified GCE sensor (5×10^{-4} – 5×10^{-2} M) [8] with real time detection.

According to the present study, for the selective detection of F^- a negligible degradation in the sensor response is experienced cycle by cycle. The electrical characterizations of various set of sensors were repeated and the results were repeatable, which justifies the selectivity and reliability aspect of the demonstrated sensors. Furthermore, the lifetime estimation of the fabricated sensor for the selective detection of F^- is found stable for at least 7 days or beyond.

4. Conclusions

This work demonstrates a cost effective, selective molecular sensor based on GO/Al (μ -IDE)/p-Si for detection of aqueous F^- in presence of Cl^- , Br^- , NO_3^- anions. The proposed sensor is tested for F^- anion concentration in the range of 0.1–10 ppm. The selectivity of the sensor is examined in presence of F^- at 1 ppm and Cl^- , Br^- , NO_3^- each at 50 and 100 ppm with a lifetime estimate of at least 7 days or beyond. The GO/Al (μ -IDE)/p-Si sensor results in very small change in sensing current in absence of F^- while a large change in sensing current is noticed in presence of F^- . Hence, proves the selectivity of the sensor towards F^- . Thus, the low cost, low power GO/Al (μ -IDEs)/p-Si based sensor shows great potential for ultrasensitive and selective detection of F^- present in aqueous solution.

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Biographies



Mahesh Soni was born on April 26, 1988 in Durg (Chhattisgarh, India). He received bachelor's (B.E.) degree in electronics & telecommunication from C. S. V. T. U, Bhilai (C.G.), India in 2010 and master's (M.Tech) in VLSI DESIGN from NIT Jaipur in 2012. He is currently pursuing Ph.D. at Indian Institute of Technology (IIT) Mandi, Himachal Pradesh, India. From 2014, he is working with Satinder K. Sharma and Ajay Soni of IIT Mandi on Graphene based FETs. His research interest includes Graphene and derivatives based Field Effect Transistors (FETs), memory and sensors for next generation optimal power high performance nano electronic regime devices.



Pawan Kumar was born in Himachal Pradesh, India, in 1986. He received the B.Sc. and M.Sc. degrees from Himachal Pradesh University, Shimla, India, in 2007 and 2009, respectively, and the Ph.D. degree in physics from Jaypee University of Information Technology, Waknaghat, India, in 2015. He worked as a Senior Project Scientist with the School of Computing and Electrical Engineering, Indian Institute of Technology Mandi, Mandi, India. He is currently working as a Post-Doctoral researcher at the Research Centre for Engineering Science, Graduate School of Engineering and Resource science, Akita University, Akita, Japan. His research interests include development of high resolution scanning probe microscopy techniques, applications of scanning probe microscopy to dielectric, magnetic thin films, magnetic recording head, Lithography and chemical sensor.



Ajay Soni received Ph.D. degree from UGC-DAE Consortium for Scientific Research, Indore-(M.P), India, in 2009 on "Study of Physical Properties of Nanomaterials". From 2009 to 2011 he worked as Post-Doctoral Research Fellow at Nanyang Technological University, Singapore and from 2011 to 2013 as a Post-Doctoral Research Fellow at National University of Singapore, Singapore. He is currently an Assistant Professor in the School of Basic Sciences, Indian Institute of Technology (IIT)-Mandi, India. His current research interests includes Nanomaterials and Mesoscopic Physics, Thermoelectric and Optoelectronic Chalcogenide materials.



Satinder Kumar Sharma was born in Himachal Pradesh, India, in 1978. He received the M.Sc. degree in physics (electronic science) from Himachal Pradesh University, Shimla, India, in 2002 and the Ph.D. degree from Kurukshetra University, Kurukshetra, India, in 2007. His Ph.D. thesis was on "Silicon based gate dielectric materials for VLSI/ULSI technology." From 2007 to 2010, he was a Postdoctoral Fellow at the DST Unit on Nanosciences and Nanotechnology, Department of Chemical Engineering, Indian Institute of Technology (IIT) Kanpur, Kanpur, India. He was a member of the faculty at the Electronics and Microelectronics Division, Indian Institute of Information Technology, Allahabad, India, from 2010 to 2012. He is currently an Associate Professor with the School of Computing and Electrical Engineering, IIT Mandi, Mandi, India. His current research interests include microelectronics circuits and system, CMOS device, fabrication and characterization, nano/microfabrication and design, polymer nanocomposite, sensors, photovoltaic, and self-assembly.