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Preparation of a Highly Conductive Seed Layer for Calcium Sensor Fabrication with Enhanced Sensing Performance

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KEYWORDS: Zinc oxide, iron oxide nanoparticles, highly conductive, seed layer, field-effect-transistor, calcium sensor, high sensitivity, real sample analysis

ABSTRACT: Seed layer plays a crucial role to achieve high electrical conductivity and ensure higher performance of the devices. In this study, we report fabrication of a solution-gated field-effect transistor (FET) sensor based on zinc oxide nanorods (ZnO NRs) modified iron oxide nanoparticles (α -Fe₂O₃ NPs) grown on a highly conductive sandwich-like seed layer (ZnO seed layer/Ag nanowires/ZnO seed layer). The sandwich-like seed layer and ZnO NRs modification with α -Fe₂O₃ NPs provide excellent conductivity and prevent possible ZnO NRs surface damage from low pH enzyme immobilization, respectively. The highly conductive solution-gated FET sensor employed the calmodulin (CaM) immobilization on the surface of α -Fe₂O₃-ZnO NRs for selective detection of calcium ions (Ca²⁺). The solution-gated FET sensor exhibited a substantial change in conductance upon introduction of different concentrations of Ca²⁺ and showed high sensitivity (416.8 μ A cm⁻² mM⁻¹) and wide linear range (0.01-3.0 mM). As well, the total Ca²⁺ concentration in water and serum samples were also measured. Compared to the analytically obtained data, our sensor was found to measure Ca²⁺ in the water and serum samples accurately, suggesting a potential alternative for Ca²⁺ determination in water and serum samples, specifically used for drinking/irrigation and clinical analysis.

Minerals in small concentrations are essential for the regular functioning of various life forms and maintaining the ecosystem. However, higher concentrations accumulations of these minerals execute toxic effects to various organisms as well as disrupt the ecosystem balance. Especially, calcium ion (Ca²⁺) is an important element for biological activity including human life. Several times abundant calcium is found in drinking water, which is in the ionic form. After consumption of such ionic form Ca²⁺, these get easily absorbed in the gastrointestinal tract.¹⁻³ Hence, it becomes crucial to measure its concentration at low detection limits. Various techniques e.g. spectroscopic techniques⁴⁻⁶, liquid chromatography⁷, electrochemical⁸, potentiometric⁹⁻¹¹, microfluidic system^{12,13}, and photometry¹⁴ have been proposed for the mineral ion detection. However, most of these methods include process like sampling and also are time-consuming and costly tasks for products based on the aqueous solution. Additionally, large system size, complex instrumentations, sensitivity, and selectivity are the major limitations. Among all, potentiometric FET sensors have advantage over other methods due to the charge accumulation on the channels semiconducting material between source-drain (S-D) electrodes, which gets affected by external fields.¹⁵⁻¹⁷ The potentiometric ion sensors containing a membrane as the main component can selectively transfers certain species over others.¹⁸⁻²⁰ These membranes have the ionophore which transfer specific ions in complex samples for selective detection. Mostly, polyvinyl chloride (PVC) membrane is used to integrate calcium ionophore or valinomycin on to it for functional-

izing nanostructured materials used as channels between S-D.²¹⁻²⁴

The designs of FET devices are mainly based on nanostructure owing the capability to form channels between S-D on the dielectric layer. ZnO is a versatile nanomaterial with exciting features i.e. semiconducting, piezoelectric, and biosafe nature.²⁵⁻²⁸ Also, the size and shape/morphology of ZnO nanostructures can be controlled easily, which influence on the properties of ZnO nanomaterial.²⁹⁻³³ Their applications for sensors fabrication have attracted considerable interest of the researchers because of easy synthesis, large surface-to-volume ratio, low-cost, and high electron-transfer rates.³⁴⁻³⁶ Recently, directly grown ZnO nanostructure on electrode surface has been successfully used for enhanced enzyme immobilization, which resulted in good stability, reproducibility and excellent sensing performance of biosensors.^{30,38-41}

Herein, we have fabricated a highly conductive solution-gated FET sensor using zinc oxide nanorods (ZnO NRs) modified iron oxide nanoparticles (α -Fe₂O₃ NPs) grown on a sandwich-like seed layer (ZnO seed layer/Ag nanowires/ZnO seed layer) for calcium (Ca²⁺) detection for the first time. The ZnO NRs grown on highly conductive seed layers were further modified with α -Fe₂O₃ NPs, which helps to overcome the surface damage, improve the conductivity and enhance the CaM immobilization. Thus, the as-fabricated sensors demonstrate a remarkable high sensitivity, wide-linear detection range and selectivity toward Ca²⁺, which are ascribed to the CaM immobilized α -Fe₂O₃-ZnO NRs grown on the highly conductive seed layer. Moreover, the fabricated FET sensors were suc-

cessfully applied for Ca^{2+} determination in water and serum samples.

EXPERIMENTAL SECTION

Chemicals. Zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\geq 98\%$), hexamethylenetetramine ($\text{C}_6\text{H}_{12}\text{N}_4$, HMTA, 99%), 0.5% silver nanowires (Ag NWs; diam. = 115 nm, L = 20–50 μm) in isopropyl alcohol suspension, iron(III) nitrate nonahydrate ($\geq 98\%$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), calmodulin (CaM) bovine (lyophilized powder, $\geq 98\%$), tris buffered saline (TBS) tablet, Nafion, calcium chloride (CaCl_2 , 1 M in H_2O) solution, lithium chloride (LiCl , $\geq 99.0\%$), sodium chloride (NaCl , $\geq 99.5\%$), potassium chloride (KCl , $\geq 99.0\%$), cadmium chloride (CdCl_2 , 99.99%), magnesium chloride (MgCl_2 , $\geq 98\%$), and human blood serum (H4522) sample were obtained from Sigma-Aldrich. Sylgard 184 A and Sylgard 184 B were purchased from Sewang Hitech to make polydimethylsiloxane (PDMS). Ultrapure water (deionized (DI)) with $\sim 18 \text{ M}\Omega \text{ cm}$ resistivity purified by Milli-Q plus system (Millipore Co.) was used.

Fabrication of a Highly Conductive Seed Layer Based Solution-gated FET. The highly conductive seed layers were fabricated between pre-deposited source-drain (S-D) silver (Ag) electrodes on the cleaned glass substrates. Scheme 1 shows the fabrication process of a highly conductive solution-gated FET based calcium sensor. First, Ag electrodes of $\sim 100 \text{ nm}$ thickness were deposited on a defined area (masked were used to cover unwanted area) by sputter. The S-D electrodes were designed to have the 0.5 cm channel length. After that, ZnO seed layer was deposited by sputter using a mask. Then, a thin layer of Ag NWs was spin-coated at 4000 rpm speed for 20 s using purchased Ag NWs solution. Finally, ZnO seed layer was again sputtered over a thin layer of Ag NWs/ZnO seed layer and used for growing ZnO NRs. The ZnO NRs were grown on the highly conductive seed layers by simple solution process at low temperature. Same molar of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.03 M) and HMTA (0.03 M) were dissolved in 50 mL DI water and heated in a Pyrex glass bottle for 4h at 80°C after dipping the seeded substrates upside down. After completion of the reaction, the ZnO NRs grown substrates were washed to remove impurities.

Before immobilization of CaM, the as-grown ZnO NRs were modified with $\alpha\text{-Fe}_2\text{O}_3$ NPs to overcome the surface damage of ZnO NRs during CaM immobilization or experiment operated in strong acidic/alkaline environments. To modify the ZnO NRs with $\alpha\text{-Fe}_2\text{O}_3$ NPs, in 20 mL DI water 0.06 gm $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was dissolved and ZnO NRs grown electrodes were dipped for 2 min in the above solution.⁴² As a result, ZnO NRs were covered with iron(II) hydroxide ($\text{Fe}(\text{OH})_2$), were further annealed to make well crystallized $\alpha\text{-Fe}_2\text{O}_3$ NPs which is thermodynamically more stable than the iron(II) hydroxide. This process is important, as it not only provides stability to the ZnO NRs but also improves the CaM immobilization efficiency and conductivity of the devices. Then, the CaM solution was prepared by diluting in TBS solution (5 mg/mL) and CaM solution was immobilized onto the surface of $\alpha\text{-Fe}_2\text{O}_3$ -ZnO NRs by a physical adsorption method. After dropping CaM solutions on $\alpha\text{-Fe}_2\text{O}_3$ -ZnO NRs, the electrode was kept at 4°C for 12h, which allowed CaM to be absorbed onto the $\alpha\text{-Fe}_2\text{O}_3$ -ZnO NRs surfaces. After drying at room temperature, the sensing device was rinsed with deionized water to remove extra CaM. In the last step, CaM/ $\alpha\text{-Fe}_2\text{O}_3$ -ZnO NRs surface was covered with 1 μL of 0.5 wt%

Scheme 1. Fabrication process of a highly conductive solution-gated FET based calcium sensor.

Nafion solution to avoid possible CaM leakage foreign interferences. Similarly, two devices (i.e. ZnO NRs/ZnO seed layer/glass substrate (Device 1) and $\alpha\text{-Fe}_2\text{O}_3$ -ZnO NRs/ZnO seed layer/glass substrate (Device 2)) were fabricated using same fabrication process after immobilization of CaM on ZnO NRs and $\alpha\text{-Fe}_2\text{O}_3$ -ZnO NRs surface to compare the sensing performance and validate the role of $\alpha\text{-Fe}_2\text{O}_3$ NPs, ZnO NRs, and Ag NWs.

Characterizations. The structural investigation of as-synthesized ZnO NRs and $\alpha\text{-Fe}_2\text{O}_3$ -ZnO NRs were performed using FESEM (Carl Zeiss, supra-40 VP) and high-resolution TEM (HRTEM, JEOL-JEM-2010 with CCD camera). The elemental chemical composition was determined by the TEM-EDX-line scan. The chemical states were analyzed by XPS (M/s. AXIS-NOVA, Kratos Inc) with Al-K (1486.6 eV) at 150W. The electrical properties of fabricated highly conductive solution-gated FET sensor were evaluated at air-ambient conditions using a semiconductor parameter analyzer (HP 4155A) after connecting fabricated FET sensor with a data acquisition system. To determine the sensing properties of the fabricated sensors, change in drain current (I_D) was monitored while extending gate voltage range (V_G) at a fixed drain-source (V_{DS}) voltage of 0.1 V. V_G was applied through reference gate electrode (Ag/AgCl) dipped in the solution containing analyte. Sensing experiments were performed in 0.05 M TBS solution at an ambient environment. Calcium concentration in serum sample (obtained from Sigma-Aldrich) was measured using our optimized calcium sensor FET and further validated with iCAP Q ICP-MS (inductively-coupled plasma mass spectrometers; Thermo Scientific; Germany) measured value. Serum sample was 10 times diluted before ICP-MS analysis.

RESULTS AND DISCUSSION

The general morphology of every step characterized by FESEM is shown in Figure 1. The cross-sectional FESEM image of as-deposited ZnO seed layer showed a smooth and uniform thickness all over the deposited area (Figure 1a). Top-view FESEM image (Figure 1b) showing a uniform Ag NWs spin-coated over the deposited ZnO seed layer. Figure 1c shows FESEM image of as-grown ZnO NRs on the highly

Figure 1. FESEM images showing (a) cross-sectional view of ZnO seed layer deposition by sputter on cleaned glass substrate between Ag (S-D); surface views of (b) spin coated Ag NWs on seed layer and (c) ZnO NRs on ZnO seed layer deposited by sputter; (d) cross section of ZnO NRs grown on seed layer, (e) surface views of α -Fe₂O₃ NPs-ZnO NRs, and (f) CaM immobilized on ZnO NRs modified with α -Fe₂O₃ NPs.

conductive seed layer. These nanorods have the diameter in the range of 80-90 nm, smooth surface, grown in high density, and were vertically-aligned to the substrate (Figure 1d). Also, an array like ZnO NRs on the surface is due to the presence of Ag NWs between ZnO seed layers. After coating ZnO NRs with α -Fe₂O₃ NPs, the surface of ZnO NRs becomes noticeably rough as they are decorated with numerous Fe₂O₃ NPs (Figure 1e). Furthermore, the FESEM image in Figure 1f clearly indicates that the CaM was evenly and abundantly immobilized on α -Fe₂O₃-ZnO NRs surface.

To gain further insights into the crystalline nature and composition of α -Fe₂O₃-ZnO NRs, TEM, HRTEM and associated diffraction techniques were employed (Figure 2). Low and high-resolution TEM image of a single ZnO NR modified with α -Fe₂O₃ NPs (Figure 2a-c) reveals that the ZnO NR are uniformly coated with α -Fe₂O₃ NPs. The TEM-EDX showing the corresponding elemental mapping image of a single ZnO NR modified with α -Fe₂O₃ NPs (Figure 2d) and TEM-EDX-line scan Zn (Figure 2e), O (Figure 2f) and Fe (Figure 2g), respectively. TEM-EDX-line scans revealed the elemental distribution and confirm the presence of Fe on the surface of ZnO NRs.

XPS was used to investigate the surface structure and composition of ZnO NRs and α -Fe₂O₃-ZnO NRs, as shown in Figure 3. The survey spectra of ZnO NRs (black) and α -Fe₂O₃-ZnO NRs (blue) are shown in Figure 3a. The high-resolution spectra of the Zn species in ZnO NRs and α -Fe₂O₃-ZnO NRs demonstrated two peaks at 1020.16 eV (2p_{3/2}), 1043.61 eV (2p_{1/2}) and 1021.6 eV (2p_{3/2}), 1044.6 eV (2p_{1/2}), respectively.⁴³ Moreover, Figure 3b shows that the intensities of the Zn 2p peaks clearly decreased after ZnO NRs modification with α -Fe₂O₃ NPs, which corresponds to the decrease in the amount of ZnO NRs on the surfaces due to the covering of α -Fe₂O₃ NPs. Also, the binding energy of ZnO NRs was slightly increased after α -Fe₂O₃ NPs modification. The deconvoluted

spectra of O 1s peak showed two individual peaks (Figure 3c). For ZnO NRs, the lower binding energy peak positioned at 529.5 eV was attributed to the lattice oxygen and this peak is related to the Zn-O chemical bonding in pristine ZnO, whereas the higher binding energy peak positioned at 530.6 eV was due to surface hydroxyl oxygen.⁴⁴ The deconvoluted spectra of α -Fe₂O₃-ZnO NRs showed similar lower and higher binding

Figure 2. TEM analysis of ZnO NRs modified with α -Fe₂O₃ NPs; Low- (a-b) and high-resolution (c) TEM images, (d) the corresponding elemental mapping image showing TEM-EDX-line scan of Zn (e), O (f) and Fe (g), respectively.

Figure 3. XPS spectral analysis of ZnO NRs and α -Fe₂O₃ NPs modified ZnO NRs showing full scan (a) and corresponding deconvoluted peaks in the high resolution spectra of various elements present, i.e., Zn 2p (b), O 1s (c), and Fe 2p (d).

energy peaks. Notably, the intensity of lower binding energy was increased while the intensity of higher binding energy peak was slightly decreased. This provides sufficient indication of the Fe-O bond formation in the α -Fe₂O₃-ZnO NRs. Figure 3d shows the high-resolution spectra of Fe species in pure ZnO NRs and α -Fe₂O₃-ZnO NRs. Pure ZnO NRs, shows no peaks of Fe. However, after modifying ZnO NRs with α -Fe₂O₃ NPs, Fe 2p_{3/2} and Fe 2p_{1/2} peaks were noticed at 710.95 eV and 724.5 eV, respectively. The presence of the Fe 2p satellite peak at ~731 eV confirms the Fe³⁺ state of the iron oxide product.⁴³

Before analyte measurement of fabricated FET sensors, the Ag S-D electrodes were PDMS passivated (only leaving the active area of sensor) to reduce the leak current. This step also eliminates the effect of metal-nanorods contact region and makes sure that the conductance change originates from the α -Fe₂O₃-ZnO NRs. Moreover, the uniqueness of our sensor is its highly conductive seed layer. This is confirmed by I - V measurement of only ZnO seed layer and sandwich-like seed layer (Figure 4). The sandwich-like seed layer resulted in very high current response compared to only ZnO seed layer, which is due to the introduction of Ag NWs between the seed layers. Thus, the electrons generated on the surface of α -Fe₂O₃-ZnO NRs pass directly through the highly conductive seed layer to

Figure 4. (a) I - V characteristics of only ZnO seed layer and sandwich-like seed layer (ZnO seed layer/Ag nanowires/ZnO seed layer), cross-sectional FESEM image of ZnO seed layer (b), and sandwich-like seed layer (c). Inset shows the schematic of seed layer deposited on the glass substrate.

Figure 5. (a) Side-view illustration of constructed highly conductive seed layer based calcium sensor FET, (b) Typical I_D - V_G responses of calcium sensor FET without and with 0.1 mM of Ca²⁺ in 0.05 M TBS solution (pH 7.6), (c) I_D - V_G responses of calcium sensor FET with increasing calcium concentration in 0.05 M TBS solution (pH 7.6) and (d) corresponding calibration plots in log scale.

the electrodes. Figure 5a shows the schematic of the constructed highly conductive seed layer based calcium sensor FET set-up. To evaluate the response of fabricated highly conductive solution-gated FET sensor device, the sensor response (I_D) is recorded in an optimized and constant potential range in the absence/presence of 0.1 mM of Ca²⁺ in 0.05 M TBS solution (pH 7.6). As shown in Figure 5b, the current value substantially increases in the presence of Ca²⁺ compared to that without Ca²⁺. This increase in current is due to the binding affinity of Ca²⁺ for the CaM, which is calcium binding multifunctional regulatory protein. The presence of Ca²⁺ would change the surface voltage of the sensing area thus affects the drain current (I_D) with increasing gate voltage range (V_G). Hence, increasing calcium concentration would lead the change in I_D response.

Further to explore the sensing properties of highly conductive solution-gated FET sensor, the I_D - V_G responses of the sensor were carried out with increasing calcium concentration in 0.05 M TBS solution (pH 7.6). The values of the current increases from lower to higher concentrations i.e. 0.01-5.0 mM, as shown in Figure 5c. However, the noticeable current changes were at a higher potential range (i.e. 1.0 - 2.0 V). Further, the calibration curve was plotted after taking an average current in the potential range spanning from 1.0 to 2.0 V (Figure 5d). This calibrated curve was utilized to calculate the sensitivity and linear range, which are the important parameters of any sensing device. The logarithmic plot of current response vs. Ca²⁺ concentration yields a linear behaviour (0.01-3.0 mM) with a high regression coefficient value of 0.9878, indicating a high degree of accuracy. The sensor showed a high sensitivity of 416.8 μ A cm⁻² mM⁻¹ with a low limit of detection (LOD) of ~5 nM, respectively, determined from the slope of current-concentration plot. The LOD was estimated using formula i.e. LOD=3.3(standard deviation/slope). These results indicate that the fabricated FET sensing device effectively detects Ca²⁺, owing to extraordinary high carrier mobility of α -Fe₂O₃-ZnO NRs through high conductive seed layer.

Table 1. Comparison of sensing performance of our FET based calcium sensor with previously developed calcium sensor FETs.

FET Sensor	Sensitivity	Linear range (mM)	LOD (nM)	Ref.
DB18C6 ionophore /ZnO nanorods/Ag wire	-	0.001-1	-	22
Phosphotyrosine/indium nitride film/silicon substrate	-	0.001-100	1000	45
CaM/Zn ₃ Ta ₂ O ₅ stoichiometric thin films/aluminium/silicon substrate	17.1 μ A/M	0.001-100	1000	46
Fluo-4-AM probe dye/single-walled carbon nano-tube/titanium/gold substrate	-	0.0001-1	0.1	47
CaM/ZnO NRs/ZnO seed layer/glass substrate	3.525 μ A cm ⁻² mM ⁻¹	0.1-2.5	~100	This work
CaM/ α -Fe ₂ O ₃ -ZnO NRs/ZnO seed layer/glass substrate	17.6 μ A cm ⁻² mM ⁻¹	0.01-1	~16	This work
CaM/ α -Fe ₂ O ₃ -ZnO NRs/ZnO-Ag NWs-ZnO seed layer/glass substrate	416.8 μ A cm ⁻² mM ⁻¹	0.01-3	~5	This work

Figure 6. FESEM images of ZnO NRs/ZnO seed layer/glass substrate (a) and α -Fe₂O₃-ZnO NRs/ZnO seed layer/glass substrate based FET devices along with their calibrated sensing response curves measured after CaM immobilization.

Figure 7. (a) I_D - V_G responses of calcium sensor FET showing response to 0.5 mM of each monovalent and divalent cations such as Li⁺, Na⁺, K⁺, Ca²⁺, Cd²⁺, and Mg²⁺ in 0.05 M TBS solution (pH 7.6); and (b) calibrated histogram plot, where response of Ca²⁺ was set as 100%.

Figure 8. I_D - V_G responses of calcium sensor FET showing response of water sample obtained from the factory measured with 10 sensors (a) and calibrated plot showing Ca²⁺ content in the water sample compared with data obtained from ICP-MS analysis (b). Error bars showed the SD for three measurements with same electrode.

Additionally to understand the roles of each material used to fabricate calcium sensor with enhanced sensing performance, two more FET sensing devices were fabricated without using Ag NWs. Two FET devices (i.e. ZnO NRs/ZnO seed layer/glass substrate (Device 1) and α -Fe₂O₃-ZnO NRs/ZnO seed layer/glass substrate (Device 2)) were fabricated after immobilization of CaM on ZnO NRs and α -Fe₂O₃-ZnO NRs surface. Figure 6 shows the FESEM images of ZnO NRs/ZnO seed layer/glass substrate (a) and α -Fe₂O₃-ZnO NRs/ZnO seed layer/glass substrate based FET devices along with their calibrated sensing response curves measured after CaM immobilization with increasing calcium concentration. The calculated sensing performances of these devices were compared with the highly conductive sandwich-like seed layer in Table 1. Sensitivity, linear range, and LOD of the highly conductive sandwich-like seed layer based FET were better than other devices (Table 1). Improvement in the sensing performance of highly conductive sandwich-like seed layer based FET can be attributed to the α -Fe₂O₃ and Ag NWs, which provided greater surface area for CaM immobilization and fast transfer of electrons through highly conductive Ag NWs, respectively. While comparing sensing performance with previously reported FET based calcium sensors (Table 1), sensitivity of our FET sensor is better. However, Kao *et al.* (2012) and Lee *et al.* (2014) reported better linear ranges but LOD is ~200 times high, which may be not good for samples containing low calcium concentrations.^{45,46}

To investigate the binding affinity of highly conductive solution-gated FET sensor toward metal cations, the I_D - V_G responses were measured to 0.5 mM of each monovalent and divalent cations such as Li⁺, Na⁺, K⁺, Ca²⁺, Cd²⁺, and Mg²⁺ in 0.05 M TBS solution (pH 7.6). Figure 7a and 7b reveal that the Ca²⁺ gives the highest current response, due to the highest binding affinity of the Ca²⁺ with CaM. Further to determine the selectivity of the sensor, 0.5 mM of each monovalent and divalent cations i.e. Li⁺, Na⁺, K⁺, Ca²⁺, Cd²⁺, and Mg²⁺ were dissolved together in 0.05 M TBS solution (pH 7.6) and response of the sensor was measured, which gives almost similar response to that of without these interfering ions. This further suggests that our fabricated sensors are selective for Ca²⁺ measurements in the presence of other metal ions.

The applicability and reliability of highly conductive solution-gated FET sensor were checked. To do so, the water sample from the agriculture factory was collected and measured by our sensor. As shown in Figure 8a, all 10 sensors showed an almost similar response. The calculated Ca²⁺ concentration in water sample was 0.89 ± 0.02 mM (Figure 8b).

Table 2. Measurement of Ca ²⁺ concentration in real samples.		
Sample	FET Sensor	ICP-MS analysis
Water from agriculture factory	0.89 ± 0.02 mM	0.90 mM
Human blood serum	1.11 ± 0.07 mM	1.14 mM

Additionally, to demonstrate the application of as-fabricated FET based calcium sensor in clinical analysis. The I_D - V_G response of our fabricated calcium sensor FET was measured after dropping 20 μ L human serum (H4522; Sigma-Aldrich) on the active area of sensor. From obtained data, the calcium concentration in serum sample was calibrated and is presented in Table 2. Further to validate the performance of our sensor, the determined results were compared with those measured by the ICP-MS analysis. The values measured by the developed sensor are nearly same to that of analytically measured value. This agreement demonstrates the potential practical application of solution-gated FET sensor for Ca^{2+} detection.

CONCLUSIONS

A highly conductive solution-gated FET sensor has been fabricated using a sandwich-like high conductive seed layer for calcium detection. The ZnO NRs grown on the highly conductive seed layers were further modified with $\alpha\text{-Fe}_2\text{O}_3$ NPs, which helps to overcome the surface damage, improve the conductivity and CaM immobilization efficiency. The fabricated sensors showed a remarkable selective response to calcium with high sensitivity in wide-linear detection range. This result is ascribed to CaM immobilized $\alpha\text{-Fe}_2\text{O}_3$ -ZnO NRs grown on highly conductive seed layer. In addition, FET sensors were successfully used for calcium detection in water and serum samples, thus proving a useful platform not only to monitor calcium in drinking and irrigation water but also could be used to monitor the calcium levels in patients suffering from hypocalcemia or hypercalcemia.

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Notes

The authors declare no competing financial interest.

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