Photoelectrochemical detection of calcium ions based on hematite nanorod sensor substrates

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ABSTRACT

α-Fe₂O₃ (hematite) thin films have been shown to be a robust sensor substrate for photoelectrochemical imaging with good stability and high spatial resolution. Herein, one-dimensional (1D) hematite nanorods (NRs) synthesized via a simple hydrothermal method are proposed as a substrate, which provides nanostructured surfaces with enhanced photocurrent responses, good stability and excellent spatial resolution for potential imaging applications. The photoelectrochemical sensing capability of hematite NRs was demonstrated by a high pH sensitivity without modification and by an amperometric response to calcium ions (Ca²⁺) when modified with a thin ion-sensitive membrane.
KEYWORDS

α-Fe₂O₃ (hematite) nanorods, photoelectrochemical sensing, calcium ion (Ca²⁺) sensing, light-addressable potentiometric sensor, light-activated electrochemistry

INTRODUCTION

Calcium ions (Ca²⁺) have a key role in both the intra-cellular and extra-cellular signalling of cells that affect every aspect of cellular life such as gene expression, protein secretion and cell adhesion, differentiation, proliferation, apoptosis and exocytosis. Moreover, the monitoring of Ca²⁺ concentrations is of significance in organo-transplantation, plaque fluid, water quality, soils and fertilizers. Light-addressable potentiometric sensors (LAPS) have been reported to detect Ca²⁺ by measuring the potential shift in illuminated areas, offering the possibility of sensing with spatial resolution that could solve the problem of limited active sites in ion-sensitive field-effect transistor (ISFET) and overcome the geometry limitation in microelectrode arrays (MEAs). LAPS are passive devices as they use electrolyte-insulator-semiconductor structures that do not allow a faradaic current to pass. Instead, they measure ac photocurrents that are strongly affected by the charge of ion-selective films placed on the semiconductor surface.

In contrast to LAPS, photoelectrochemical imaging using metal oxide semiconductor substrates such as ITO or α-Fe₂O₃ (hematite) are based on the measurement of local light-induced faradaic currents due to the oxidation of hydroxide ions in the solution. Hematite thin films have been shown to be robust sensor substrates for
photoelectrochemical imaging of living cells due to their high stability and good spatial resolution\textsuperscript{7}. It is anticipated that ion-sensing capability could be developed by surface modification. However, the planar hematite thin film of 200 nm thickness used previously may be not able to produce sufficient photocurrents for ion-sensing if coated with a polymeric ion-selective membrane. That is because hematite intrinsically suffers from a short charge carrier lifetime \textsuperscript{8}, a mismatch between the short hole diffusion length (2-4 nm) and long photon penetration length (~120 nm at $\lambda = 550$ nm) \textsuperscript{9}, a relatively low absorption coefficient (order of $10^{3}$ cm\textsuperscript{-1}), requiring at least a 400–500 nm thick film for optimal light absorption \textsuperscript{10}. Nanostructuring of the hematite planar film to aligned nanorods (NRs) has been reported to improve the photocurrent response as the charge carriers are channelized, facilitating hole transport to the interface which minimizes recombination of charge carriers \textsuperscript{11}. Moreover, the substrate with nanostructured rough surface is believed to enhance the film adhesion due to additional mechanical interlocking.

In this work, hematite NRs synthesized via a simple hydrothermal method are proposed as substrate for photoelectrochemical ion-sensing. The bare NRs showed high pH sensitivity and the polymeric membrane modified NRs exhibited an amperometric response to Ca\textsuperscript{2+} with a different mechanism to LAPS device. A high spatial resolution of the hematite NRs was determined by imaging a polymer dot, which reveals the potential of using this system to study ion-channel activities in cell culture in the future.
EXPERIMENTAL

Materials

Fluorine doped tin oxide (FTO) glass (15 Ω/ sq.) was purchased from Solaronix SA, Switzerland. All other chemicals were purchased from Sigma-Aldrich. All solutions were prepared using ultrapure water (18.2 MΩ·cm) from a Milli-Q water purification system (Millipore, USA).

Sample preparation

Hematite nanorods were synthesized on FTO via an adjusted hydrothermal method. Briefly, FTO glass was cut into 1 cm × 1 cm pieces and were subsequently cleaned for 10 min each with acetone, ethanol, and ultrapure water in an ultrasonication bath. After blowing dry with nitrogen gas, the FTO substrate was transferred to a Teflon-lined stainless steel autoclave (50 mL capacity) with 20 mL aqueous solution of FeCl₃·6H₂O and NaNO₃ at pH 2 (set by HCl). The autoclave was sealed and maintained at 100 °C for 6 h. After the autoclave cooled down to room temperature naturally, the FeOOH film was rinsed with copious water and blown dry with nitrogen. Finally, the as-prepared FeOOH film was calcined at 550 °C for 2 h and 750 °C for 20 min to give crystalline α-Fe₂O₃ nanorods. For comparison, hematite planar thin film samples were synthesized based on our previous work. Poly(methyl methacrylate) (PMMA, average M.W. 120000) was dissolved in methoxybenzene to form a 20 wt % solution. A PMMA dot was drop coated on hematite NRs and naturally dried before measurement.
The ion-sensitive membrane was prepared following a previously reported recipe \(^ {13, 14}\): 120 mg polyvinyl chloride (PVC), 10 mg of dibutyl phthalate (DBP) and 10 mg dibenzo-18-crown-6 (DB18C6) in 5 mL tetrahydrofuran (THF). The mixture was spin-coated on the hematite NRs at 3000 rpm for 1 min. The resulting samples were conditioned in a 0.1 M CaCl\(_2\) solution for 48 h before the test.

**Material characterisation.**

The surface and cross-sectional morphology of hematite nanorods were characterised using a scanning electron microscope (SEM, FEI Inspect F). Ultraviolet–visible (UV-vis) spectra were obtained using UV–vis spectrometer (PerkinElmer, Lamda 950). X-ray photoelectron spectroscopy (XPS) was carried out by Nexsa XPS system (Thermo Scientific, UK), XPS data were collected and analysed by Avantage (Thermo Scientific) software. The X-ray diffraction (XRD) analysis was carried out using a PANalytical X’Pert Pro diffractometer configured for grazing incidence X-ray diffraction (GIXRD) with Cu K\(\alpha\)1 radiation. The water contact angle measurement was conducted using a Drop Shape Analysis System (Krüss DSA100, Germany). Topographic imaging was carried out using an atomic force microscope (AFM, Bruker Dimension Icon, UK). Mott–Schottky plots and impedance spectra were recorded in Dulbecco’s Phosphate Buffered Saline (DPBS) solution (pH 7.4) with an Autolab PGSTAT30/FRA2 (Windsor Scientific Ltd, UK) using a platinum electrode and an Ag/AgCl electrode as the counter and reference electrodes, respectively. A sinusoidal modulation of 10 mV in amplitude was used at frequencies from 0.1 Hz to 10 kHz.
Linear sweep voltammetry

Chopped light linear sweep voltammetry (LSV) was carried out in DPBS solution (pH 7.4) using an Autolab PGSTAT30/FRA2 with the same three-electrode system as for impedance measurements. A diode laser (λ = 405 nm, max 50 mW), chopped in 10 s intervals was used as a light source while recording the LSV curves, and the scan rate was 5 mV/s.

Photoelectrochemical sensing and imaging

The experimental setup for photocurrent measurements (Figure S1, Supporting Information) has been described elsewhere. In brief, a diode laser (BioRay™ Coherent, λ=405 nm, max. power =50 mW) was used for photocurrent excitation. After being collimated by a custom-made spatial filter, the laser beam was manipulated by an analogue mirror (Mirrorcle Technologies, Inc., USA) and was focused using an objective lens with a correction ring (Nikon, numerical aperture 0.6) to scan the back surface of the sample for imaging. Photocurrents were measured with an MFLI lock-in amplifier (Zurich Instruments) with a platinum electrode and an Ag/AgCl (3 M KCl) electrode acting as the counter and reference electrodes, respectively. Optical images were taken with a digital CMOS camera (ORCA-Flash4.0 LT, Hamamatsu Photonics Ltd, UK). The system was controlled and photocurrents were recorded using a custom-designed program written in LABVIEW.
RESULTS AND DISCUSSION

Hematite nanorod characterisation

The morphology of hematite nanorod films was characterised by SEM and TEM. SEM images of the as-prepared FeOOH and annealed α-Fe₂O₃ are shown in Figure 1a and 1b, respectively. Hematite nanorods were arranged in uniform arrays which were aligned perpendicularly to the FTO substrate. The thickness of the layer was 503.6 ± 35.7 nm estimated from the cross-sectional SEM image (Figure 1c). This morphology could offer direct electrical pathways for photogenerated carriers and effectively boost electron-hole separation thus improving the photoelectrochemical properties. A bright-field TEM image of hematite nanorods is shown in Figure 1d, which displays well-defined nanorods of 7.6 ± 1.3 nm in diameter self-assembled as a bundle of 78.9 ± 4.4 nm in diameter. Figure 1e shows a high-magnification TEM image of α-Fe₂O₃ nanorods and a representative high-resolution TEM (HRTEM) image taken from the hematite nanorods. The lattice fringes are observed with a spacing of ~ 3.7 Å, which agrees well with the (012) lattice spacing of hematite. The selected area electron diffraction (SAED) pattern (Figure 1f) reveals the high poly-crystalline nature of α-Fe₂O₃ nanorods with observable diffraction rings corresponding to crystallographic planes of hematite (JCPDS 33-0664).
Figure 1. Top-view SEM images of (a) as-prepared FeOOH, (b) annealed α-Fe₂O₃ nanorods; (c) Cross-sectional view of α-Fe₂O₃ nanorods on FTO substrate. (d) Bright-field TEM image of α-Fe₂O₃ nanorods, (e) High-magnification TEM image of α-Fe₂O₃ nanorods, inset: a high-resolution TEM (HRTEM) image taken from the as-obtained α-Fe₂O₃ nanorods, (f) Selected area electron diffraction (SAED) pattern of α-Fe₂O₃ nanorods.
Figure 2. (a) XRD pattern of as-prepared $\beta$-FeOOH (akaganeite) and annealed $\alpha$-Fe$_2$O$_3$ (hematite) on FTO substrate. (b) Raman spectrum of hematite NRs on FTO substrate.

XRD analysis (Figure 2a) confirms that the as-prepared nanorods were $\beta$-FeOOH (akaganeite, JCPDS 34-1266), which were then converted into $\alpha$-Fe$_2$O$_3$ (hematite, JCPDS 33-0664) via annealing. The strongest (110) diffraction peak indicates that these hematite nanorods have a preferred [110] direction vertical to the substrate, which implies that they were grown along the [110] axis. Hematite with [110] orientation has been reported to have an anisotropic conductivity that is four orders of magnitude higher and better facilitates charge collection of photo-excited charge carriers along the 1-D nanostructures $^{17, 18}$. Raman spectrum of hematite NRs (Figure 2b) displays well-established hematite bands ($2A_g + 5E_g$) located at 222, 244, 289, 406, 497, 605 cm$^{-1}$ $^{19}$. An additional peak at 662 cm$^{-1}$ is possibly due to the presence of nanocrystals $^{20}$. The absence of Raman peaks for $\beta$-FeOOH further demonstrates the complete conversion of $\beta$-FeOOH into $\alpha$-Fe$_2$O$_3$ after calcination $^{21}$.
The surface chemistry of the hematite NRs was revealed by XPS, which confirms the presence of Fe$^{3+}$, O$^{2-}$ and Sn$^{4+}$ in the lattice and hydroxyl groups (-OH) at the surface, and the absence of iron in the XPS spectra of the Ca$^{2+}$ sensitive layer modified hematite NRs indicates complete coverage of the NRs with the polymer layer (Figure S2). A water contact angle of 33.7 ± 2.1° confirmed the hydrophilic character of the NRs surface (Figure S3). The topography of the hematite NRs was characterised by AFM (Figure S4), showing a root-mean-square (RMS) roughness of ~74.2 nm. The optical absorption of hematite NRs was characterised using UV–Vis spectroscopy (Figure S5). A direct bandgap of 2.1 eV was obtained confirming the feasibility of photocurrent excitation using 405 nm laser illumination. A Mott–Schottky plot revealed a donor density of $6.95 \times 10^{17}$ cm$^{-3}$ and a flat band potential of 0.11 V vs. Ag/AgCl for hematite NRs (Figure S6). The charge transfer resistance for hematite NRs determined with electrochemical impedance spectroscopy (EIS) was about 5.6 times lower compared to that of hematite thin films demonstrating that charge transfer at the interface is more effective for NRs (Figure S7).

**Photocurrent performance of hematite nanorods**

The photocurrent performance of hematite NRs is illustrated and compared with that of a planar hematite thin film reported previously in Figure 3. Figure 3a shows the chopped light LSV in pH 7.4 DPBS. Hematite NRs and thin films exhibited similar currents at potentials lower than 0.6 V vs. Ag/AgCl. However, a significantly higher photocurrent was observed for the NRs at potentials above 0.6 V. The enhanced photoactivity was associated with the high conductivity along the [110] axis and
increased number of active sites due to the NRs structure\textsuperscript{17,22} and the high catalytic performance of the hematite (110) facet\textsuperscript{16}. The photocurrent–voltage (\(I-V\)) curves measured with a focused laser beam modulated at 10 Hz in pH 7.4 DPBS using PEIS setup are shown in Figure 3b. Higher photocurrent values were obtained for the NRs above 0.6 V, reaching 150 nA at 1.2 V compared to 58 nA for the thin film. Figure 3c shows the current-frequency curves measured at 1 V with a focused laser beam in pH 7.4 DPBS. NRs yielded considerably higher net current until the frequency increased to 500 Hz, while at frequencies higher than 500 Hz, there is no significant difference in net photocurrent. Although both samples can be used for imaging at 10–1000 Hz, hematite NRs are the material of choice for pursuing higher photocurrent at low frequencies. Figure 3d depicts the photocurrent-time (\(I-t\)) curves measured at 0.8 V with a focused laser beam modulated at 10 Hz in pH 7.4 DPBS. Both samples were stable over 10 min indicating good reliability in photoelectrochemical imaging.
Figure 3. Comparison of photocurrent responses between hematite NRs and hematite planar thin film: (a) LSV curves measured in pH 7.4 DPBS solution with an Autolab potentiostat. (b) I-V curves measured with a focused laser beam modulated at 10 Hz in pH 7.4 DPBS using PEIS setup. (c) Photocurrent-frequency curves measured with a focused laser beam in pH 7.4 DPBS. (d) I-t curves measured with a focused laser beam over 600 s. (e) Photocurrent image of a PMMA dot measured at 1.0 V and 1 kHz with a focused laser beam, (f) x-axis line scan across the edge of the PMMA dot.
and a lateral resolution of 2.7 μm was determined from the FWHM of the first derivative of the line scan.

Photocurrent imaging using hematite NRs

Figure 3e shows the photocurrent image of a PMMA dot deposited onto the surface of hematite NRs measured at a modulation frequency of 1 kHz with a bias of 1.0 V. The polymer dot was clearly visible in the photocurrent image showing lower photocurrents compared to blank surface area owing to the high impedance of the polymer. For lateral resolution measurement, a photocurrent line scan across the edge of the polymer film was conducted with a focused laser beam (Figure 3f). A resolution of 2.7 μm was obtained from the full width at half maximum (FWHM) of the first derivative of the line scan, which is comparable to the resolution of ITO (2.3 μm) irradiated with 405 nm laser and is better than the resolution of InGaN (7 μm).

Photoelectrochemical sensing using hematite NRs

pH Sensitivity of hematite NRs

To investigate the pH sensitivity of hematite NRs, photocurrent-voltage (I-V) curves were recorded at a frequency of 10 Hz a series of phosphate buffer solutions (pH 3–9) supplemented with 0.1 M KCl using the PEIS setup. Figure 5a shows that the photocurrent increased with increasing pH in the pH range of 3–9, which reflects the enhanced oxidation reaction of hydroxide ions at higher pH. A mixed mechanism of ion exchange in a surface layer with hydroxyl (-OH) groups and redox reactions was
previously suggested for semiconducting oxides. For hematite NRs, a linear relationship between the applied voltage and pH was observed with a high sensitivity of 60.5 mV/pH (Figure 5b), which could be ascribed to a large number of active sites of the hematite NR structure, indicating the great potential of high-resolution pH imaging using hematite NRs for biochemical applications.

Figure 4. (a) $I-V$ curves of hematite NRs measured in different pH buffer solutions. 
(b) a linear fitting shows the pH sensitivity of hematite NRs.

Calcium ion sensitivity of hematite NRs coated with ion-selective PVC coating

The morphology of Ca$^{2+}$ sensitive layer modified hematite NRs is shown in Figure S8. Instead of a thick layer, a continuous polymer film was formed following the contour of NRs and filling the gaps between them, which provides the opportunity of ion sensing with faradaic electrochemistry. To explore the Ca$^{2+}$ sensing properties of the sensor, $I-V$ curves were recorded at different concentrations of CaCl$_2$ (0.1 M KCl as supporting electrolyte) with pH around 6.02 ± 0.03 at a modulation frequency of 1 kHz. At potentials lower than 0.7 V, the order of the $I-V$ curves is in agreement with a
potentiometric response. However, this response was relatively small (12.5 mV/decade) and was not reproducible from one device to another. At potentials higher than 0.9 V, the photocurrent increased with the calcium ion concentration from 1 μM to 10 mM (Figure 5a). Figure 5b shows the calibration curve of this amperometric response plotted using an average photocurrent for each concentration at a potential of 1 V. The diameter of solvated calcium ions (7 Å) is too large to be accommodated in the cavity of DB18C6 (4 Å), but the high charge on the oxygen atoms of DB18C6 allows the complexation of Ca\(^{2+}\) with DB18C6, thus a PVC film with DB18C6 has previously shown good selectivity to calcium ions in an ion selective electrode \(^{14}\). While the uncoated hematite device clearly showed a mixed potentiometric and amperometric response mechanism to pH, for the PVC coated sensor, a potentiometric response could be expected as the insulating properties of PVC can block Faradaic currents making this into a LAPS device. However, this only applies to low potentials. At higher potentials, a pure amperometric response was observed. As more calcium ions bind to DB18C6, the concentration of counter ions, including hydroxide ions, in the film increases thus enhancing the oxidation reaction of hydroxide ions at the hematite surface (see schematic diagram in Figure 6).

Selectivity of the hematite NRs based Ca\(^{2+}\) sensor was examined against magnesium (Mg\(^{2+}\)), potassium (K\(^{+}\), 0.1 M NaCl as supporting electrolyte) and sodium (Na\(^{+}\)) ions with the same concentration as the Ca\(^{2+}\) (Figure 5c). Significantly higher photocurrents were observed with Ca\(^{2+}\) owing to the high binding affinity of the Ca\(^{2+}\) with DB18C6 and there is no observable response towards Mg\(^{2+}\), K\(^{+}\) and Na\(^{+}\). A good
reversibility was shown in the time trace of photocurrent responses in Ca$^{2+}$-containing solutions with different concentrations (Figure 5d). Photocurrents increase with the Ca$^{2+}$ concentration and can return to their original levels after several washes of the electrolyte cell with deionised water. Figure S9 shows I-V curves of three sensors each measured three times in 1 mM CaCl$_2$ solution. All the measurements showed an almost identical response indicating good reliability and stability due to the good stability of the hematite substrate and the rough surface of NRs enhancing the adhesion of PVC membrane. This is an advantage over PVC-coated silicon sensors which show poor adhesion between PVC membrane and silicon. A control experiment was conducted by measuring a bare hematite NR sample (Figure S10a); no response to Ca$^{2+}$ was found confirming the Ca$^{2+}$ sensitivity was derived from the coating. The Ca$^{2+}$ sensitive PVC membrane was coated on hematite thin film for comparison; small photocurrent values and high noise level make it unsuitable for sensor application (Figure S10b).
Figure 5. (a) I-V curves of hematite NRs measured at different Ca$^{2+}$ concentrations and (b) corresponding calibration curve. (c) Photocurrent responses of hematite NRs-based Ca$^{2+}$ sensor towards different ions. (d) Time trace of the photocurrent responses in Ca$^{2+}$-containing solutions with different concentrations measured at a potential of 1 V.
Figure 6. Schematic diagram of the modified hematite NRs for the photoelectrochemical sensing of Ca^{2+}.

CONCLUSIONS

Hematite NRs aligned vertically to the FTO substrate fabricated by a hydrothermal method were studied as a platform for photoelectrochemical imaging and sensing. Hematite NRs showed a significantly increased (about 2.6 times at 1.2 V) photocurrent under irradiation of a focused 405 nm laser compared to a hematite planar film with good stability. The photocurrent imaging of a polymer dot with a
high spatial resolution of 2.7 μm was achieved. Hematite NRs displayed a pH sensitivity of 60.5 mV/pH over pH range 3 to 9 without surface modification indicating a mixed potentiometric and amperometric response mechanism. When modified with a Ca$^{2+}$ sensitive PVC membrane, hematite NRs showed an amperometric response towards Ca$^{2+}$ rather than the potentiometric response measured with traditional LAPS devices and displayed good selectivity over Na$^+$, K$^+$ and Mg$^{2+}$. The ion selective film showed excellent adhesion on the rough hematite NR surface compared to traditional silicon-based LAPS substrates. In the future, the Ca$^{2+}$ sensitivity of the hematite NRs sensor in conjunction with its imaging capabilities could be used to study ion-channel activities in cell culture through real-time photocurrent imaging. It is envisaged that a multifunctional/multiplexed platform that can detect various analytes spatiotemporally can be achieved by further modification. The successful utilization of nanostructured semiconductors for photoelectrochemical imaging and sensing tremendously expands the range of photo-responsive nanomaterials that could be explored in this field.

Supplementary material contains:

- The Schematic of the photoelectrochemical imaging system setup
- XPS spectra of hematite NRs and the Ca$^{2+}$ sensitive layer modified-hematite NRs
- Water contact angle of hematite NRs
- AFM images of hematite NRs
- UV-vis spectrum of hematite NRs and Tauc-plot
• Mott–Schottky plot of hematite NRs
• Electrochemical impedance spectra of hematite NRs and equivalent circuit
• SEM image of Ca²⁺ sensitive layer modified hematite NRs
• I-V curves of three sensors each measured three times in 1 mM CaCl₂ solution.
• Control experiments of bare hematite NRs and Ca²⁺ sensitive layer modified hematite planar film in Ca²⁺ sensing

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CRediT authorship contribution statement

Declaration of competing interest

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.
REFERENCES


Supporting information

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Figure S1. Schematic of the photoelectrochemical imaging system (PEIS) setup.

The surface electronic structure and chemical states of hematite NRs and Ca\textsuperscript{2+} sensitive layer modified-hematite NRs were investigated by XPS measurements. The survey spectra (Figure S2a) confirm the presence of Fe, O, Sn and adventitious C at the surface of hematite NRs and the presence of C, O Cl at the modified surface. The high-resolution spectrum of Fe2p of hematite NRs (Figure S2b) contains two distinct
peaks at binding energies of ~711.1 eV for Fe 2p3/2 and ~724.4 eV for Fe 2p1/2, and two shake-up satellites at ~719.3 eV and ~733.4 eV were observed as indicators of Fe3+ in Fe2O3. However, there is no detectable peak at this range for the modified hematite NRs which confirms the full coverage of the polymer layer (Figure S2b).

O1s spectrum of the hematite NRs (Figure S3c) displays an intense peak associated with the “O2−” of the crystalline network at 530.1 eV and a peak located at 531.9 eV which is attributed to hydroxyl groups at the surface. While there is a main O1s peak for the modified surface associated with the C-O appears in dibenzo-18-crown-6 (DB18C6) and dibutyl phthalate (DBP), and a small peak related to C=O of DBP (Figure S3c). Peaks with spin-orbit splitting (Δ=1.6 eV) in Cl2p spectrum (Figure S2d) of the modified surface confirms the assignment of organic Cl from polyvinyl chloride (PVC).

Figure S2. XPS spectra of hematite NRs and Ca2+ sensitive layer modified-hematite NRs: (a) survey scans, (b) high-resolution Fe2p scans, (c) high-resolution O1s scans, (d) high-resolution Cl2p scan.
Figure S3. Water contact angle of hematite NRs.

Figure S4. (a) AFM top view image and (b) 3D map of hematite NRs.
Figure S5. UV-vis spectrum of α-Fe₂O₃ nanorods and inset Tauc-plot.

From a Mott–Schottky plot of a hematite film (Figure S6), a donor density of \(6.95 \times 10^{17} \text{ cm}^{-3}\) and flat band potential \((U_{FB})\) of 0.11 V vs. Ag/AgCl were calculated based on the Mott–Schottky equation (equation S1):

\[
\frac{1}{C^2} = \frac{1}{e\varepsilon\varepsilon_0 N_d} \left( U - U_{FB} - \frac{KT}{e} \right)
\]  

(S1)

where \(C\) is the space charge layer capacitance, \(e\) is the electron charge, \(\varepsilon\) is the relative permittivity of hematite (\(\varepsilon = 80\))^3, \(\varepsilon_0\) is the permittivity of vacuum, \(N_d\) is the donor density, \(U_{FB}\) is the flat band potential, \(U\) is the applied potential at the electrode, \(K\) is the Boltzmann's constant, and \(T\) is the operation temperature.

![Mott–Schottky plot of hematite NRs recorded at 1 kHz using an Autolab PGSTAT30/FRA2 with a sinusoidal voltage perturbation of 10 mV in pH 7.4 DPBS.](image)

**Figure S6.** Mott–Schottky plot of hematite NRs recorded at 1 kHz using an Autolab PGSTAT30/FRA2 with a sinusoidal voltage perturbation of 10 mV in pH 7.4 DPBS.
EIS measurements were conducted to investigate the kinetics of charge transfer at the electrode surface. Figure S7a shows the Bode plots of a hematite nanorod sample and a hematite thin film sample measured at 0.8 V under illumination. Hematite NRs exhibit lower impedance than thin film sample at low frequencies, which indicates NRs have higher charge transfer efficiency. Figure S7b shows the equivalent circuit model with two time constants for fitting the EIS data, which includes the electrolyte resistance $R_s$, a resistance representing the trapping of holes in surface states $R_{\text{trap}}$, and a charge transfer resistance $R_{\text{ct,ss}}$, and two constant phase element (CPE) $Q_{\text{sc}}$ and $Q_{\text{ss}}$ associated with space charge capacitance and surface state capacitance respectively. The values of frequency power $n$ for the CPE are closer to 1 (perfect capacitor) for hematite thin films compared than those values for NRs, which reflects the inhomogeneous distribution of reaction rate or higher surface roughness due to the NR structure. The calculated values of the circuit elements are presented in Table S1; a higher $Q_{\text{ss}}$ for NRs compared to thin film indicates more charging of the surface states with hematite NRs, and about 5.6 times lower $R_{\text{ct,ss}}$ for hematite NRs represents a more effective charge transfer from surface states to the electrolyte.
Figure S7. (a) Bode plots of hematite NR and thin film electrodes measured at 0.8 V in the dark and under illumination in pH 7.4 DPBS (dots - measured values, lines - equivalent circuit fit); (b) Equivalent circuit model used for fitting the impedance spectra.

Table S1. Parameters calculated from the equivalent circuit.

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Figure S8. SEM image of Ca²⁺ sensitive layer modified hematite NRs.

Figure S9. I-V curves of three sensors each measured three times in 1 mM CaCl₂ solution.
Figure S10. (a) I-V curves of a bare hematite NRs measured in CaCl₂ solution. (b) I-V curve of a PVC-coated hematite thin film measured in 10 mM CaCl₂ solution.

References


