Electroactive biofilms (EABs) have received considerable attention, because of their electrochemical connections with the substrate, which can be employed for harvesting energy from organic waste and converting waste into valuable chemicals.1−3 The electrochemical properties of biofilms primarily contribute to the presence of some specific strains (i.e., Shewanella and Geobacter) that are able to exchange electrons with a solid substrate.4,5 So far, two main mechanisms have been distinguished for the electron transfer between EABs and the substrata, including direct electron transfer (DET) via bacterial outer-membrane redox proteins and indirect electron transfer via redox metabolites.6 Nevertheless, present understanding of the specific interactions between electrochemically active microbes and the solid electron acceptors is far from complete. In the case of the DET, available data suggest that surface-localized redox proteins in the EABs, such as outer membrane (OM) c-type cytochromes (OM c-Cyts), multicopper proteins, and pilin proteins, are responsible for the electron transfer,7−10 but the identity of the redox proteins wiring EABs to electrodes is still challenging.

Spectroelectrochemical techniques have been proven to be useful in revealing the microbial electron-transfer process by correlating voltammetry data with spectral characteristics of the EABs. Various spectral techniques such as ultraviolet–visible light (UV-vis), Raman, and infrared adsorption spectroscopy could be linked with electrochemical analysis to monitor the redox status of redox-active proteins in EABs, from which valuable information about the extracellular electron transfer (EET) process can be obtained.11 However, the bulky optics that are necessary for these spectroscopic techniques limit their applications for in situ monitoring of various hard-to-reach environments such as field wastewater, soils, and sediments.

Surface plasmon resonance (SPR) spectroscopies are desirable techniques for in situ measurement of electronic states of the chemical and biological molecules. When integrated with electrochemistry (EC), electrochemical surface plasmon resonance (EC-SPR) offers a promising way to simultaneously explore optical and electrochemical properties of chemical and biological matrix accompanying redox reactions. For example, Baba et al. coupled EC with SPR to probe the electrochromic and redox properties of conductive...
polymer thin films.15 Yao et al. quantified the orientation changes of ferrocenyldalkanethiol self-assembled monolayers during electrochemical oxidation using an EC-SPR sensor.16 Boussaad et al. used EC-SPR to survey conformational and electronic changes of purified c-Cyts protein.17 However, the EC-SPR system was constructed with a bulky prism configuration, and it has never been applied to measure the optical and electrochemical properties of a living biofilm accompanied by redox transformation in situ.

Herein, we report the first application of EC-SPR for in situ measuring of the electrochemical activity of EABs. The electrochemical surface plasmon resonance optical fiber sensor (EC-SPR-OFS) proposed here consists of a gold-coated tilted fiber Bragg grating (TFBG) imprinted in a commercial single-mode fiber core, in which the nanometric-scale gold coating over the fiber surface offers the simultaneous detection of both the electrochemical information (electrochemical current) and the optical information (plasmon wave). Such a sensor is a cost-established free-space optics (i.e., bulky prism configurations) for high-sensitivity biochemical detections due to the high-efficiency light-matter interaction.18 Moreover, its tiny size makes it feasible to be inserted into various hard-to-reach environments for in situ detection (avoiding the need to bring biosamples inside an instrument) either as a hand-held probe or as a set of remotely operated devices along a fiber-optic cable, especially for environmental monitoring over the urban and suburban areas.19 By using such a hybrid technique (electrochemical and plasmonic techniques), the different spectral responses of redox species of the EABs, in real time and in situ, have been achieved, providing a prospect for the use of this technique for monitoring the redox electrochemistry of the EABs.

■ MATERIALS AND METHODS

Sensor Configuration and System. The EC-SPR-OFS proposed in this work is composed of a compact plasmonic fiber-optic sensing system combined with a bioelectrochemical system. The plasmonic optical fiber sensing probe performs the
optical detection function (Figure 1) and it also works as an electrode in the electrochemical system (Figure 2). The right inset of Figure 1 presents the detailed configuration of the plasmonic fiber-optic sensing probe, which consists of a tilted fiber Bragg grating (TFBG) imprinted in the core of a commercial single-mode fiber provided with a nanometric gold coating. TFBGs benefit from two unique features: one is the strong polarization selectivity of the excited cladding modes and other is the high-density comb of narrowband spectral resonances. When a linearly polarized light is launched with its polarization parallel to the tilt plane of grating (P-polarization, Figure 1), the electric field of the cladding modes is ∼100% polarized in the radial direction (i.e., in the TM polarization relative to the metal coating), to ensure the strongest SPR excitation. The entire plasmonic fiber-optic sensing probe is very compact, with a size of 20 mm in length and 0.125 mm in diameter (the left inset of Figure 1). Measurements of the plasmon wave properties by the transmission spectrum of the TFBG provide the in situ optical information for EET of EABs. The plasmon waves of the gold-coated TFBG are hybrid waves that have intense field localization at the outer surface of the metal film (represented by the red waves shown in the right inset of Figure 1).

**Bacterial Culture.** Geobacter sulfurreducens strain PCA (ATCC51573) was subcultured using a standard anaerobic medium at 30 °C. This anaerobic medium contains (per 1 L): 0.2 g of NH4Cl, 0.38 g of KCl, 0.069 g of NaH2PO4·H2O, 0.1 g of MgSO4·7H2O, 0.04 g of CaCl2·2H2O, and 10 mL of a mineral solution. Acetate was used as an electron donor at a concentration of 1.0 g/L. The medium was adjusted to pH 6.8 prior to the addition of 1.8 g/L NaHCO3, and purged with N2/CO2 (80/20, v/v). G. sulfurreducens mutants were cultured under the same conditions as the wild-type strain. Shewanella oneidensis MR-1 was cultured and inoculated to the electrochemical cell, as previously reported. A mixed culture obtained from a well-maintained bioelectrochemical system was inoculated to the electrochemical cell to form a mixed culture EAB. E. coli was also cultured in 50 mL of LB broth with gentle shaking. Here, a grating tilt of 20° was chosen to maximize the sensing response in aqueous solutions with refractive indices of 1.32–1.34.

Thin noble-metal sheaths (here, gold has been used) have been successfully deposited on the optical fiber by sputtering technology. To achieve a high-quality coating, two issues must be addressed. One is to improve the adhesion of the gold to the surface of fiber glass. Here, we used a 2–3 nm thickness of chromium sandwiched between the fiber surface and the gold film. The second is to ensure a uniform thickness of the gold film over the entire fiber surface (this is very important to the SPR excitation). The traditional flat-plane sputtering technique is not suitable for cylindrical fibers, because sputtering is a directional process and the target is fixed. Therefore, in order to avoid thickness nonuniformities, the fiber was rotated along its axis during the sputtering process. This design ensures a very uniform nanometric coating over the fiber surface. The current work was carried out with a gold thickness of ∼50 nm.

**SPR Excitation and Spectral Characteristics.** The plasmon waves provide the in situ information for EET of EABs. They are hybrid waves that have intense field localization at the outer surface of a metal film deposited on an optical fiber support. When the refractive index of the outer medium is smaller than that of the solid support, a propagating wave incident from the support side can be totally reflected internally at the support metal boundary but phase-matched one transfer

\[
X_i = 0.5 \left\{ \frac{A}{\exp\left(\frac{E}{kT}\right)}(E - E_{f1,i}) + B \right\} + 0.5 \left\{ \frac{C}{\exp\left(\frac{E}{kT}\right)}(E - E_{f2,i}) + D \right\}
\]

where \(E_{f1,i}\) and \(E_{f2,i}\) are the formal potentials of the cytochrome proteins, respectively; \(n_1\) and \(n_2\) are the number of electron exchanged in the reaction, respectively; \(X_i\) is the reduced or oxidized fraction of the cytochrome proteins; \(A\) and \(B\) are the maximum difference intensity between the fully oxidized and the fully reduced state, respectively; \(B\) and \(D\) are the respective offsets; \(R\) is the gas constant, \(F\) represents the Faraday constant, \(T\) is the reaction temperature, and \(E\) is the electrode potential.
to a quasi-Plasmon excitation at the outer boundary of the metal. In order for this coupling to occur, the incident wave must be radial at the fiber external boundary (i.e., P-polarization), to transfer energy to a plasmon wave on the metal surface. Meanwhile, the thickness of the metal layer must be thin enough (50 nm thickness for the optimal thickness for SPR excitation) to let some light tunnel across. Evidence of SPR in the spectrum for this polarization is the disappearance of the cladding mode resonances (as the clear attenuation near 1520 nm of the red transmission shown in Figure 3) due to the coupling of the cladding mode energy to the very lossy surface plasmon wave at these wavelengths. When the other direction of the input polarized light is used, i.e., S-polarization, the electric field is tangent to fiber surface and no SPR occurs (as the black transmission shown in Figure 3).

■ RESULTS AND DISCUSSION

Biofilm Formation and Characterization. Prior to EC-SPR-OFS measurements, initially well-cultured G. sulfurreducens cells were inoculated into the bioelectrochemical cell by polarizing the optical fiber working electrode at 0 V vs SCE to form a biofilm on the gold-coated optical fiber electrode, using a multichannel potentiostat (Model CHI1000C, China). CA and CV measurements were performed with the gold-coated optical fiber as the working electrode (surface area = 0.4 cm²). Scanning electron microscopy (SEM) images confirmed the formation of the biofilm on the optical fiber. As shown in Figure 4a, a smooth optical fiber surface was observed before inoculation. After 10 days of culturing, microbial cells forming a biofilm were clearly observed on the optical fiber (see Figures 4b and 4c).

During the biofilm formation, the electrochemical current was also recorded, which is shown in Figure 4d. After a lag phase, an electrochemical current was observed from the biofilm formed from wild-type G. sulfurreducens. In contrast, almost no current was obtained from the abiotic control. For comparison, mutant strains were also inoculated into the bioelectrochemical cell, which showed a small current generation from the strain with the omcS gene deleted (ΔomcS) and almost no current from the mutant strain with omcB, omcS, omcT, omcE, and omcZ genes deleted (ΔomcBESTZ). Previous studies have demonstrated that omcB, omcS, and omcZ are the key redox proteins to relay electron transfer from inside the G. sulfurreducens to outside substrata. CVs under turnover and nonturnover conditions further confirmed the electrochemical activity of the EABs with a scan rate of 5 mV/s. As shown in Figure 4e, sigmoidal CVs were observed within the biofilms that resulted from wild-type and omcS deletion mutant in the presence of acetate, indicating the oxidation of acetate by these biofilms. In contrary, almost no catalytic currents were observed from the biofilms resulting from the ΔomcBESTZ mutant and the abiotic optical fiber. Figure 4f presents the CVs of the biofilms under the acetate depleted condition. Redox couples with formal potentials of −0.41 and −0.49 V vs SCE (−0.17 and −0.25 V vs standard hydrogen electrode (SHE)) appeared in the CV of the biofilm with the wild-type strain. These redox peaks were assigned to omcB (outer membrane c-type Cytochrome b) and omcZ (outer membrane c-type Cytochrome Z), respectively. However, only one couple of redox peaks was observed from the biofilm with the omcS deletion mutant, and almost no redox peaks were observed from the biofilm with the ΔomcBESTZ. This confirmed that the presence of OM c-Cyts is important for the EET of the G. sulfurreducens biofilm.

Optical Response of the EABs. Accompanying the electrochemical measurements, the optical spectral responses of the plasmonic fiber-optic sensor are recorded. As shown in Figure 5a, the transmission spectra of the EAB-attached plasmonic fiber-optic sensor (inscribed with a TFBG) presents a fine comb of narrowband resonances that overlaps the spectral region where the plasmon wave absorbs some of the light (this spectral region is colored orange). These fine spectral resonances provide a unique tool to measure small shifts of the plasmon with high accuracy: when the plasmon wave spectral...
maximum moves in response to changes in the immediate vicinity of the metal surface, the amplitudes of the individual resonances of the TFBG either grow or decrease, depending whether the plasmon peak (SPR) loss gets closer or farther. With the variation of the redox state of the EAB (0, −0.4 V, and −0.8 V vs SCE), strong SPR wavelength shifts have been observed and their response varies in accordance with the applied potentials. The most accurate measure of the SPR wavelength shift is obtained by monitoring the amplitude change of a select resonance located on the short wavelength side of the SPR maximum (this resonance is identified by a red asterisk (*) and is labeled "plasmonic" in Figure 5b). The amplitude of this resonance increases when the SPR loss moves toward longer wavelengths, in response to surrounding refractive index or applied potential increases.25,26 Here, in our experiment, the amplitude of the "SPR" resonance increases ∼15 dB when the applied potential (at the gold-coated fiber working electrode) changes from 0 V to −0.8 V. The identification of the plasmonic resonance in subsequent measurements is enabled by referencing all wavelengths to the location of the core mode reflection resonance (Figure 5c), which is completely insensitive to the external environment of the fiber. Furthermore, since all resonance wavelengths have the same response to temperature shifts, the aforementioned referencing of wavelengths to the core mode resonance removes any influence of temperature on the measurements. Monitoring of the power level of the transmission spectrum near the core resonance also ensures that fluctuation of the light power level (from the light source and anywhere else in the optical path) is identified and eliminated from the measured data, thus maximizing the signal-to-noise ratio, the stability, and the reliability of the proposed sensor.

SPR Responses of the Redox Properties of the EABs under Potentiostatic Control. To further observe the SPR responses of the redox process in the EABs, detailed changes in

Figure 4. (a–c) SEM images of the gold-coated optical fibers ((a) abiotic fiber, (b) optical fiber with G. sulfurreducens biofilm, and (c) high-resolution image of the G. sulfurreducens biofilm). Electrochemical measurements of the EABs: (d) Current–time (I–t) curves of the bioelectrochemical systems with various inoculations; (e) CV scans of the EABs on the optical fibers under turnover conditions; (f) CV scans of the EABs on the optical fibers under nonturnover conditions.

Figure 5. Optical spectral responses of EAB measurement: (a) spectral response of gold-coated 20° TFBG with SPR excitations under different electrode polarizations; (b) enlarged view of the spectral change of SPR modulated cladding modes (note that the "plasmonic" cladding mode is marked by a red asterisk (*) ); and (c) enlarged view of the spectrum near the core mode reference resonance.

the SPR amplitude were measured during the EET. EC-SPR-OFS experiments were performed by employing potential jumps from the positive potentials (0 V) to the negative potentials (−0.8 V). Figure 6a shows the current response of various biofilms on the potential jumps from 0 and −0.8 V, which showed the decrease in the current generation of the EABs. A current of 4.6 μA was obtained from the wild-type G. sulfurreducens biofilm at the potential of 0 V, which was the
highest value among all \textit{G. sulfurreducens} strains. According to previous studies, the EET ability of the EABs was assigned to the activity of surface-localized redox-active proteins or bulk redox compounds, such OM c-Cyts, multicopper proteins, pilin proteins, and endogenous mediators excreted by bacteria.\textsuperscript{27−29} It is well-known that the electron states of the redox species were associated with the applied potentials at the working electrodes.\textsuperscript{30,31} When an anodic potential was applied to the EABs, the redox species in the EABs were in their oxidation states. In contrast, the redox species in the EABs were in their reduction states when a cathodic potential was applied to the EABs. Associated with the potential jumps, we found that the differential SPR amplitude obtained by subtracting the SPR amplitude between the measured potentials and 0 V was correspondingly varied. Notably, using the differential SPR amplitude (instead of absolute amplitude) can eliminate the effect of the bacterial biomass and cell viability on the measurements of the redox activity among different optic fibers and EABs. This approach can also effectively cancel out any unwanted fluctuations originating from the light source or transmission path. As presented in Figure 6b, the differential SPR amplitudes were inversely related to the current generation. Note that differential SPR amplitude of the EABs with \textit{G. sulfurreducens} mutants and other biofilms at the potential of $-0.8$ V (i.e., \textit{S. oneidensis} MR-1, \textit{E. coli}, and a mixed culture) was smaller, compared to the wild-type \textit{G. sulfurreducens} biofilm (Table 1), which can identify the lower electroactivities of biofilms. Based on these experimental results, the maximum current density ($I_{\text{max}}$) of the EABs varied linearly with the measured differential SPR amplitude ($\Delta \text{SPR}$),

$$[\Delta \text{SPR}] = 6.97 + 0.74 \times [I_{\text{max}}] \quad R^2 = 0.998$$

as shown in the right inset figure in Table 1. Note that the biocurrent flowing on the fibers may potentially influence the SPR signals. To demonstrate the relationship between the biocurrent flowing and the SPR signal of the EABs, we measured the SPR of the same mature EABs under both turnover and nonturnover conditions. As shown in Figure 7a, EC-SPR measurements were performed at three time points of the same EAB. Current generation properties of the EAB were recorded at these three time points, which showed great variations (Figure 7b). The generated currents of 3.7, 2.4, and 0.1 \textmu A were achieved at points a, b, and c, respectively, which represented different redox state of the EAB. However, the changes in the differential SPR amplitudes were almost identical (Figure 7c). This means that the variations in the

![Figure 6](image1.png)

(a) Current–potential curves of the EABs under turnover conditions; (b) potential-dependent background-subtracted SPR intensity of the EABs; (c) fraction of c-Cyts in the biofilm as a function of the potential, as determined by EC-SPR-OFS spectroscopy (the dashed lines indicate the fit to a model); and (d) the first derivative of the SPR intensity curve over the potential.

![Figure 7](image2.png)

(a) Current–time ($I$–$t$) curves of the bioelectrochemical systems with \textit{G. sulfurreducens} for a long-term operation; (b) current–potential ($I$–$V$) curves of the \textit{G. sulfurreducens} biofilm obtained at points a, b, and c in panel (a), respectively; (c) potential-dependent background-subtracted SPR amplitude of the biofilm at points a, b, and c in panel (a), respectively; and (d) potential-dependent background-subtracted SPR amplitude of the biofilm under nonturnover condition at different time intervals, showing the remarkable stability of the system for long-term operation.

Table 1. Relationship between the Maximum Current Density ($I_{\text{max}}$) and the Corresponding Differential SPR Amplitudes ($\Delta \text{SPR}$) of Various EABs (Subtraction of the SPR Amplitudes between the Applied Potential of $-0.8$ V and 0 V) Is Presented Both in the Table (Left) and the Plot (Right) (Not Including the Non-EABs, $\Delta$omcBESTZ, and \textit{E. coli})

<table>
<thead>
<tr>
<th>Biofilms</th>
<th>$I_{\text{max}}$ (\textmu A/cm$^2$)</th>
<th>Differential SPR amplitude (dB)</th>
</tr>
</thead>
<tbody>
<tr>
<td>\textit{G. sulfurreducens} (wild-type)</td>
<td>11.4 $\pm$ 0.5</td>
<td>15.5 $\pm$ 1.0</td>
</tr>
<tr>
<td>\textit{G. sulfurreducens} (\textit{Δ}omcS)</td>
<td>2.6 $\pm$ 0.4</td>
<td>9.0 $\pm$ 0.4</td>
</tr>
<tr>
<td>\textit{G. sulfurreducens} (\textit{Δ}omcBESTZ)</td>
<td>0.9 $\pm$ 0.2</td>
<td>1.4 $\pm$ 0.2</td>
</tr>
<tr>
<td>\textit{S. oneidensis} MR-1</td>
<td>5.9 $\pm$ 0.4</td>
<td>11.2 $\pm$ 0.7</td>
</tr>
<tr>
<td>\textit{E. coli}</td>
<td>0.5 $\pm$ 0.3</td>
<td>1.2 $\pm$ 0.3</td>
</tr>
<tr>
<td>A mixed culture</td>
<td>8.9 $\pm$ 0.7</td>
<td>13.6 $\pm$ 0.8</td>
</tr>
</tbody>
</table>

Figure 6. (a) Current–potential curves of the EABs under turnover conditions; (b) potential-dependent background-subtracted SPR intensity of the EABs; (c) fraction of c-Cyts in the biofilm as a function of the potential, as determined by EC-SPR-OFS spectroscopy (the dashed lines indicate the fit to a model); and (d) the first derivative of the SPR intensity curve over the potential.
differential SPR amplitudes were associated with the redox activities of the biofilms rather than the current flowing through the gold coating over the fiber surface. Note that almost identical SPR responses were achieved from the biofilm over a long time span, suggesting the remarkable stability of the constructed EC-SPR-OFS for monitoring the EABs (Figure 7d).

According to previous studies, the SPR angular shift from the immobilized redox metalloprotein in the EC-SPR system is mainly caused by the conformation changes of the redox protein (c-Cyts) in the EABs. These are, in turn, induced by the changes in the valency state of iron in heme during the redox process. In addition, the SPR angular shift can result from the refractive index difference between the reduced and oxidized forms of the bulk redox species. Thus, the EC-SPR-OFS mainly probes the presence and redox states of the redox species in the EABs, which can be further used to indirectly predict the EET ability of the EAB. As shown in Figure 6c, the contribution of the reduced components increased with the decrease of the electrode potential, and vice versa, which was obtained by normalizing the differential SPR amplitude by the differential SPR amplitude at ~0.8 V (assuming a completely reduced state), respectively. The resultant potential-dependent changes of the redox states of the EABs were then analyzed in terms of the Nernst equation.

A fit of the Nernst equation for independent redox couples to the data in Figure 6c afforded a two-electron transfer process with apparent formal potentials of −0.15 and −0.25 V vs SHE for the EAB with the wild-type strain, which are in very good agreement with the CV results. The electron transfer from G. sulfurreducens to solid electron acceptors is accomplished by a wide variety of OM c-Cyts with broad potential windows, such as omcS (from −0.36 to −0.04 V vs SHE), and OmcZ (from −0.42 to −0.06 V vs SHE). Interestingly, the broad shape of the redox potential window of the EAB with the wild-type strain is observed on the first-deviation curve of the differential SPR amplitude curve over the potential (Figure 6d), whereas a narrow shape of redox potential window was obtained from the EAB with the ΔomcS mutant, and no signals were observed from the EAB with the ΔomcBESTZ mutant. It is worth mentioning that the EET process of G. sulfurreducens biofilms was complicated and has not been fully understood yet. In addition to OM c-Cyts, Okamoto et al. revealed that efficient bacterial EET involved OM c-Cyts-bound flavins that function as a redox cofactor in the scaffold of OM c-Cyts. The formal potential of OM c-Cyts-bound flavins was observed at ~0.20 V vs SHE, which should also be included in the redox potential window of the EAB with the wild-type strain in Figure 6d. On the other hand, other surface-localized redox proteins that are also involved in the EET, such as multicopper proteins and pilin proteins, might also contribute to SPR signals. Shewanella biofilms are also well-studied EABs, which showed a similar SPR response as the Geobacter biofilms in the EC-SPR-OFS system (Table 1). It has been revealed that OM c-Cyts (OmcA and MtrC), protein-bound and bulk endogenous mediators excreted by bacteria contribute to the EET of Shewanella biofilms. Therefore, the SPR signal of this biofilm can be assigned to surface-localized redox proteins and bound or bulk endogenous mediators.

The EABs commonly vary in thickness from a few micrometers to several millimeters, which involves complex long-distance electron transfer. Two-layer bacterial aggregations have been identified in the thick EABs, including a live outer layer (nearer the solution interface) and a dead inner layer of biofilm (nearer the electrode interface). The live outer layer of biofilm has been considered to be responsible for current production and the dead inner layer has been suggested to function as an electrically conductive matrix. However, investigations are still insufficient to provide insight into the biofilm structure relative to its electrochemical properties. To date, electrochemical techniques have been primarily applied to study the EET process in EABs, yielding important insights into their redox process. However, electrochemical techniques cannot provide structural and spatial information, because they only perform a “bulk” detection in which the current or change information originates from the entire electrode surface. The EC-SPR method proposed here provides a very “localized” and “surface” detection of the inner layer of biofilm (adjacent to the electrode interface) because the SPR signals are mainly confined to a spatial thickness of ~1 μm above the surface of the gold film. To be more specific, in this case, the plasmon waves mainly propagate in the inner layer of a multilayered biofilm. In this regard, the EC-SPR-OFS measurements revealed that the inner layer of the EAB was electrochemically active during the EET, which is consistent with previous surveys. In addition, as discussed earlier, the combinations of UV-vis, Raman, and Fourier transform infrared (FTIR) spectroscopies with electrochemistry offer good opportunities for revealing the structure information of the EABs. However, free-space configurations of these conventional spectroscopies required the measurements to be performed mainly in laboratories. The inherent advantages of the proposed fiber-optic sensors include their low cost, lightweight, small size, ruggedness, and remote operation ability, making it possible for them to fully integrate with various in-field environments such as soil, sediments, and wastewaters, especially for those hard-to-reach places.

CONCLUSIONS

In summary, we have demonstrated the first electrochemical surface plasmon resonance (EC-SPR) optical absorption spectrum of electroactive biofilms (EABs) during metabolism. By implementing such a hybrid technique (electrochemical and plasmonic methods) over one compact optical fiber sensor, further understanding on how electron transfer occurs in EABs, in real time, has been achieved. This powerful technique, which is associated with mutant analysis, reveals the important role of the redox species in the extracellular electron transfer (EET), as well as the redox states of these redox species during metabolism. Benefiting from the advantages of compact size, cost-effectiveness, and simple implementation, as well as the possibility of remote operation, the proposed electrochemical surface plasmon resonance optical fiber sensor (EC-SPR-OFS) is an appealing solution for observing the electrochemical activity of biofilms developed in various natural environments.

AUTHOR INFORMATION

Corresponding Authors

*Tel.: +86 20 85221606. Fax: +86 20 85222046. E-mail: tuanguo@jnu.edu.cn (T. Guo).
*Tel.: +86 20 37300951. Fax: +86 20 87025872. E-mail: sgzhou@soil.gd.cn (S. Zhou).

Notes

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