Electronic Supplementary Information *for*

Facet-dependent reductive dissolution of hematite nanoparticles by *Shewanella putrefaciens* CN-32

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S1. Addition of materials and methods

1. Synthesis of hematite {001} and {100}

Hematite {001} was synthesized by mixing 1.64 g $FeCl_3 \cdot 6H_2O$ with 4.2 mL ultrapure water, and then 4.8 g sodium acetate was added into the solution and stirred by magnetic stirring bar for 30 min. Subsequently, the mixed suspension was placed into a 100 ml Teflon-lined stainless-steel autoclave and heated to 180 ℃ in an oven for 12 h. For hematite {100}, 4.05 g $FeCl_3 \cdot 6H_2O$ was added into 30 ml ultrapure water and stirred by magnetic stirring bar for 30 min. After stirring, 1, 2-diaminopropane was added into the suspension at 1:1 volume ratio and stirred for 30 min to make the suspension disperse evenly. Then the suspension was sealed in a 100 ml Teflon-lined stainless-steel autoclave and heated to 180 °C in an oven for 12 h. The suspensions were centrifuged and the obtained solids were washed by ultra-pure ethanol and deionized water for several times, respectively. The hematite nanoparticle powders were freeze-drying and heated at 400 °C for 2 hours to remove the residual organic solvents. After cooling down to room temperature, the solids were collected and stored at room temperature for biotransformation experiments.

2. Surface charge density and cyclic voltammetry curve measurement

For surface charge density measurement, 0.56 g hematite nanoparticle powders were dissolved in 70 ml 10 mM NaCl electrolyte solutions and sonicated for 20 min to obtain the evenly dispersed suspensions. The hematite suspensions were firstly titrated with 0.01 M HCl to pH 3.0 and then back-titrated to pH 11 with 0.01 M NaOH. During the titration process, the titration rate was set at 0.3 uL s^{-1} and the whole titration processes were conducted in a N_2 atmosphere under vigorous stirring to remove the CO_2. The surface charge density (σ, coul m^{-2}) calculated as following two equations,[1]

$$H_{ads} = C_a - C_b - [H^+] + [OH^-]$$

$$\sigma = \frac{F \beta H_{ads}}{c \beta SSA}$$

In which C_a and C_b are the concentrations of the added HCl and NaOH in the back-titration process, respectively, and $[H^+]$ and $[OH^-]$ are the concentrations of H^+ and OH^-, respectively, F is Faraday constant, c is the concentrations of Fe oxides (g L^{-1}) and SSA is the specific surface area of Fe oxides (m^2 g^{-1}). The point of zero charge (pH_{pzc}) of hematite was set at σ = 0, which was independent of the ionic strength.[2]

For DPV and Tafel curve measurements, the Pt electrode were firstly polished with 1.0 and 0.06 mm Al_2O_3 for 10 min, respectively, and washed by Milli-Q water. This process was repeated twice. Then the hematite nanoparticles dispersed in dilute Nafion solution was sonicated for 10 min and pitted onto the Pt electrode, and air-dried at room temperature. Subsequently, the Pt electrode was placed in the anoxic 30 mM PIPES buffer solution at pH 6.8. For DPV measurement, the potential was ranged from -0.6 to 0.7 eV, and both pulse period and pulse width were set to 5 s. For Tafel plot measurements, the potential was ranged from -0.8 to 0.8 eV and scan rate was 0.1 mV s^{-1}. The polarization resistance (R_p), corrosion current (I_{corr}), and corrosion potential (E_{corr}) were directly obtained by CHI 650D software. Both DPV and Tafel curve measurements were conducted in an anaerobic environment.

Before DPV and Tafel measurements, the Pt electrode should be activated with H_2SO_4 and CV curve of $K_4[Fe(CN)_6]$ should be obtained to ensure the quality of electrode.

3. Characterization of pure hematite nanoparticles and transformation products

The FTIR spectra of hematite {001} and {100} were obtained with a Bruker Vertex 70 spectrophotometer. The specific surface area of hematite {001} and {100} were determined by Brunauer-Emmett-Teller method. The Fe 2p and O 1s XPS spectra of hematite {001} and {100} were conducted on a Thermo Scientific™ K-Alpha™+ spectrometer. Before testing the target element, the binding energy C1s was used as the energy correction. The Peakfit v.4.12 software was used for the all XPS data analysis.

Bruker D8 Advance X-ray diffractometer, equipped with Lynx Eye Array detector and Cu Kα (λ = 0.154 nm) diffraction, was used to identify the purity of pure hematite nanoparticles and the compositions of transformation products at 120 h. The diffractometer tube voltage and current were operated at 40 kV and 40 mA, respectively. The scan step was 0.02° at 2° min^{-1} in the 2θ ranged from 10° to 70°. In order to prevent the interference of Fe(II) oxidation to the XRD characterization, the powder samples are firstly mixed with glycerin in an anaerobic chamber and then used for XRD analysis.

4. Time-resolved ATR-FTIR measurement

The adsorption kinetics experiments of *S. putrefaciens* CN-32 with either hematite {001} or {100} were conducted at pH 6.8 and reaction times up to 6 h. The whole experiments were performed in the absence of organic substance (e.g., lactate) to stabilize the biomass and prevent the bacterial lysis.[3] Briefly, 300 μL of 2 g L^{-1} hematite {001} or {100} suspension was evenly dropped on the horizontal ZnSe crystal and air-dried for 12 h to form a stable hematite film. The ZnSe ATR crystal was sealed in a flow cell and softly rinsed with anoxic deionized water to remove the impurities and then rinsed with 0.1 M NaCl solution at pH 6.8 for 4 fours. The flow cell rate was set at 1.0 ml min^{-1}. A background spectrum containing of the absorbance of the ZnSe crystal, hematite film and NaCl solution were collected. Subsequently, the NaCl solution was changed to anoxic CN-32 suspensions with cell density of 10^8 cells ml^{-1} in 0.1 M NaCl at pH 6.8. During the whole experiment, the anoxic CN-32 suspension pre-adjusted to pH 6.8 was stirred by a magnetic stir bar to ensure the bacteria evenly mixed, and the pH of suspension was kept at 6.8 using either 0.1 M NaOH or HCl.

The two important factors, including the rate of flow cell and the number of scans of spectrum, should be seriously considered during the ATR-FTIR measurements. The interaction between CN-32 and hematite can be influenced by the cell densities and the flow cell rate, so the number of cells was fixed at 10^8 cell ml^{-1} and flow cell rate was set as 0.5 ml min^{-1} based on the preliminary experiments to obtain continuously varying FTIR spectra within the collection time.[3, 4] In this study, in order to obtain the good quality of spectra, 256 scans were collected for each spectrum and all spectra were collected ranged from the 4000 to 800 cm^{-1} with a 4 cm^{-1} resolution. All time-resolved spectra were collected every 4 min at short term (0-60 min) and every 15 min at long term (60-360 min). The control experiment of the pure CN-32 suspensions at pH 6.8 was also conducted and the corresponding FTIR

spectrum was collected by subtracting the background spectra consisting of ZnSe crystals and 0.1 M NaCl solution at pH 6.8 from the CN-32 spectra.

5. ATR-FTIR spectra analysis

During the data analysis process, all spectra were smoothed and baseline corrected using Omnic 8.0 software, and the obtained spectra were used for the 2D-COS analysis through the 2Dshige software (Shigeaki Morita, Japan). The sequential order of spectral intensity change between two bands at ν_1 and ν_2 can be obtained from the signs of synchronous correlation peak $\Phi(\nu_1, \nu_2)$ and asynchronous correlation peak $\psi(\nu_1, \nu_2)$ based on previously principles.[5] Briefly, if $\Phi(\nu_1, \nu_2)$ and $\psi(\nu_1, \nu_2)$ have the same signs, the change in the spectral intensity at band ν_1 occurs prior to ν_2. If $\Phi(\nu_1, \nu_2)$ and $\psi(\nu_1, \nu_2)$ have the opposite signs, the order will be reversed. If $\psi(\nu_1, \nu_2)$ is zero, they will occur simultaneously. In addition, in order to better elucidate the binding mechanism of bacterial functional groups and hematite {001} or {100}, the peak fittings of selected spectra at t= 60 min and t = 360 min were performed with Peakfit v.4.12 software. The goodness-of-fit parameter was used to judge the quality of fitting results and the good fits usually require R-factor greater than 0.99.

S2. Addition of tables and figures

Table S1. The peak positions of FTIR spectra and corresponding functional groups for *S. putrefaciens* CN-32.[4]

Peak positions (cm^{-1})	Functional groups
1720-1729	C=O stretch in COOH
1652-1637	amide I: C=O stretching, -CN and -NH bending in amines
1550-1540	amide II: N-H bending, C-N stretching bending of CH_2/CH_3
1454-1482	Bending of CH_2/CH_3
1360-1450	$\upsilon_s(COO^-)$
1210-1270	P=O stretch in phosphates asymmetric and symmetric stretching of phosphate PO_2 and $P(OH)_2$
1150-950	asymmetric and symmetric stretching of phosphate PO_2 and $P(OH)_2$
1114-1118	υ(C-O-P, P-O-P), ring vibrations
1084-1094	$\upsilon_s(PO_2)$; ring vibrations; υ(C-O); P=O stretch in phosphodiester, phosphorylated proteins, and C=C vibrations of polysaccharides
1048-1078	C-OH, C-O-C, and C-C vibrations of polysaccharides
1039-1043	υ(P-OH, P-OFe)
1016-1020	υ(P-OFe), ring vibrations
962-979	fully symmetric (υ_1) stretching of PO_3 and PO_2

Table S2. Deconvoluted FTIR spectra peak positions and corresponding complexes for phosphorous functional groups during the adhesion process.[4]

Peak positions (cm^{-1})	Complexes
1150-1160	υ(P-O) of phosphoryl surface complexes
1110-1120	υ(P=O) of bridging bidentate surface complexes
1080-1085	$\upsilon_s(PO_2^-)$ of monodentate surface complexes
1045	υ(P-OFe) of monodentate surface complexes
995-1011	$\upsilon_{as}(P\text{-}(OFe)_2)$ of bridging bidentate surface complexes
950-955	υ(P-OFe) or υ(P-OH)
927-930	$\upsilon_s(P\text{-}(OFe)_2)$ of bridging bidentate surface complexes

Table S3. Signs of each cross-peak in the synchronous (φ) and asynchronous (ψ) (in the brackets) at short term (0-60 min) during the cell adhesion on hematite {001}.

	1644	1550	1446	1395	1234	1080	1048	985
1644	+(0)	+(-)	+(0)	+(0)	+(-)	+(-)	+(-)	+(-)
1550		+(0)	+(+)	+(+)	+(-)	+(-)	+(-)	+(-)
1446			0(0)	0(0)	+(0)	+(-)	+(-)	+(0)
1395				0(0)	+(0)	+(-)	+(-)	+(0)
1234					+(0)	+(-)	+(-)	+(0)
1080						+(0)	+(0)	+(0)
1048							+(0)	+(0)
985								+(0)

"0": no cross peak appears in the contour maps.

Table S4. Signs of each cross-peak in the synchronous (φ) and asynchronous (ψ) (in the brackets) at short term (60-360 min) during the cell adhesion on hematite {001}.

	1653	1556	1441	1396	1234	1082	1047	986
1653	+(-)	+(+)	+(+)	+(+)	+(+)	+(+)	+(+)	+(+)
1556		+(0)	+(0)	+(0)	+(0)	+(+)	+(+)	+(+)
1441			+(0)	+(0)	+(0)	+(0)	+(0)	+(0)
1396				+(0)	+(0)	+(0)	+(+)	+(0)
1234					+(0)	+(0)	+(0)	+(0)
1082						+(0)	+(0)	+(0)
1047							+(0)	+(0)
986								+(0)

"0": no cross peak appears in the contour maps.

Table S5. Signs of each cross-peak in the synchronous (φ) and asynchronous (ψ) (in the brackets) at short term (0-60 min) during the cell adhesion on hematite {100}.

	1643	1548	1447	1396	1234	1080	1046	983
1643	+(0)	+(-)	+(0)	+(0)	+(-)	+(-)	+(-)	+(-)
1548		+(0)	+(+)	+(+)	+(-)	+(-)	+(-)	+(-)
1447			0(0)	0(0)	0(-)	+(-)	+(-)	0(-)
1396				0(0)	+(-)	+(-)	+(-)	0(-)
1234					+(0)	+(-)	+(-)	+(-)
1080						+(0)	+(-)	+(-)
1046							+(0)	+(-)
983								+(0)

"0": no cross peak appears in the contour maps.

Table S6. Signs of each cross-peak in the synchronous (φ) and asynchronous (ψ) (in the brackets) at short term (60-360 min) during the cell adhesion on hematite {100}.

	1650	1547	1450	1396	1234	1081	1045	988
1650	+(0)	0(+)	+(-)	+(-)	+(-)	+(-)	+(-)	+(-)
1547		0(0)	-(0)	-(0)	-(0)	-(0)	-(0)	-(0)
1450			+(0)	+(-)	+(-)	+(-)	+(-)	+(-)
1396				+(0)	+(-)	+(-)	+(-)	+(-)
1234					+(-)	+(-)	+(-)	+(-)
1081						+(-)	+(-)	+(-)
1045							+(-)	+(0)
988								+(-)

"0": no cross peak appears in the contour maps.

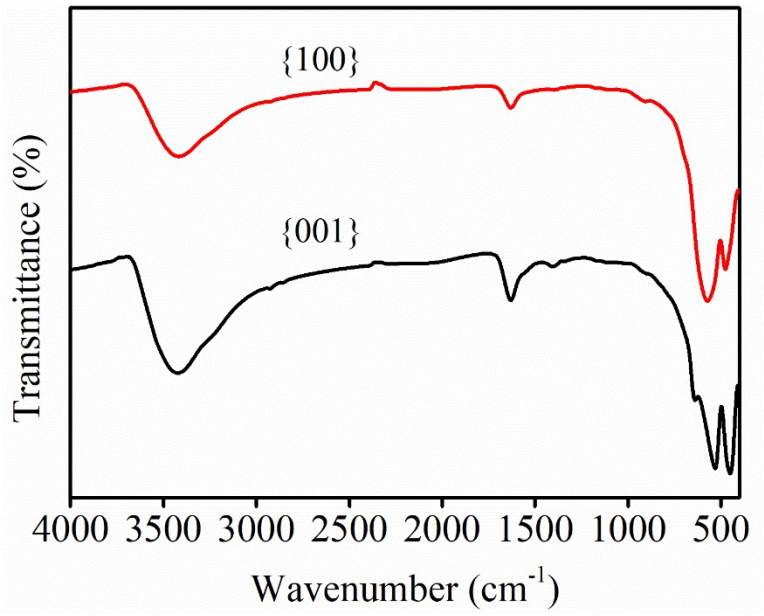

Figure S1. FTIR spectra of hematite {001} and {100}.

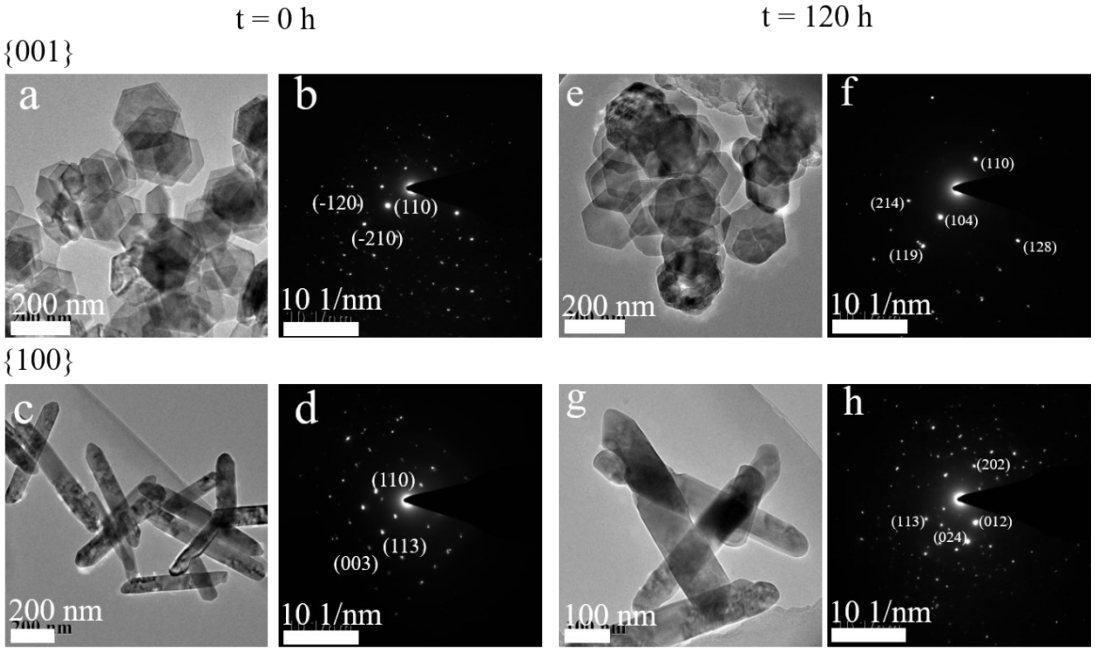

Figure S2. The TEM images and SAED patterns of hematite {001} and {100} at t = 0 h and 120 h.

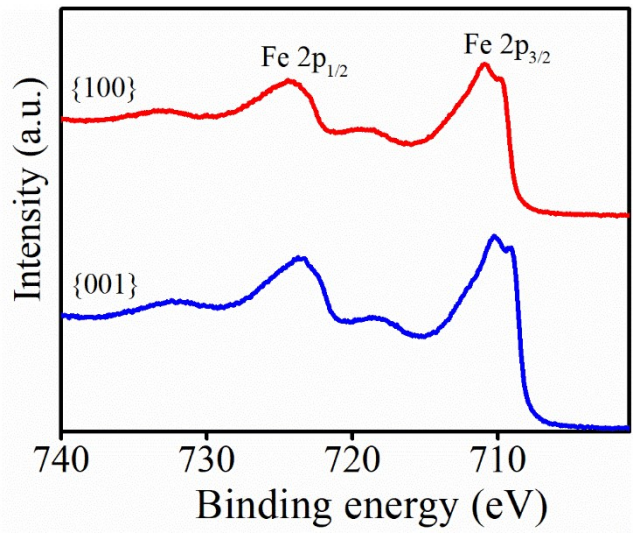

Figure S3. The Fe 2p XPS spectra of hematite {001} and {100}.

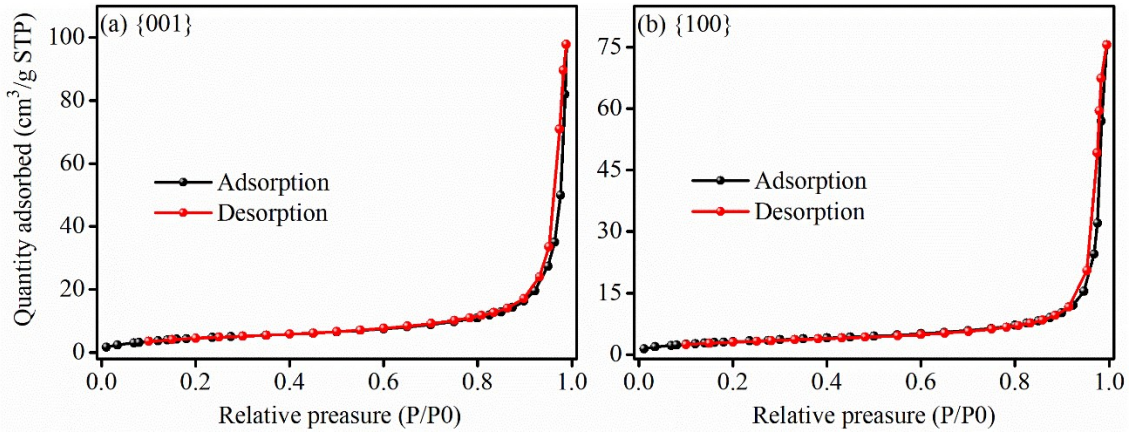

Figure S4. N_2 adsorption and desorption isotherms of hematite (a) {001} and (b) {100}.

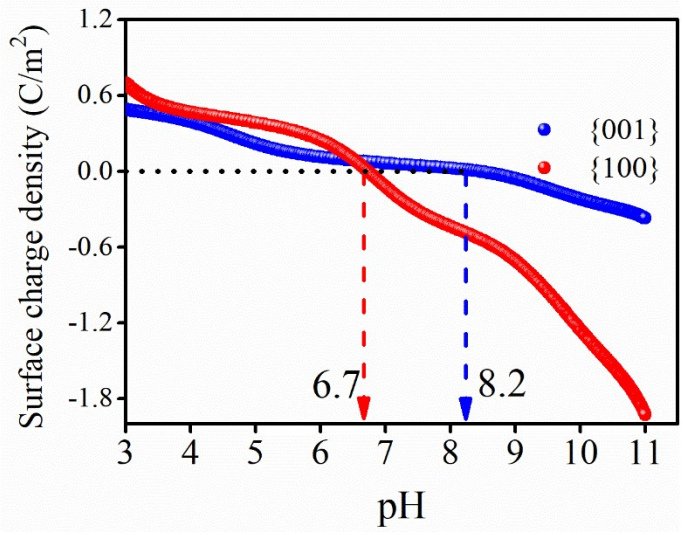

Figure S5. surface charge density of hematite {001} and {100} as a function of pH in the presence of 10 mM NaCl. The specific surface areas of hematite {001} and {100} were 18.2 and 14.0 m^2 g^{-1}.

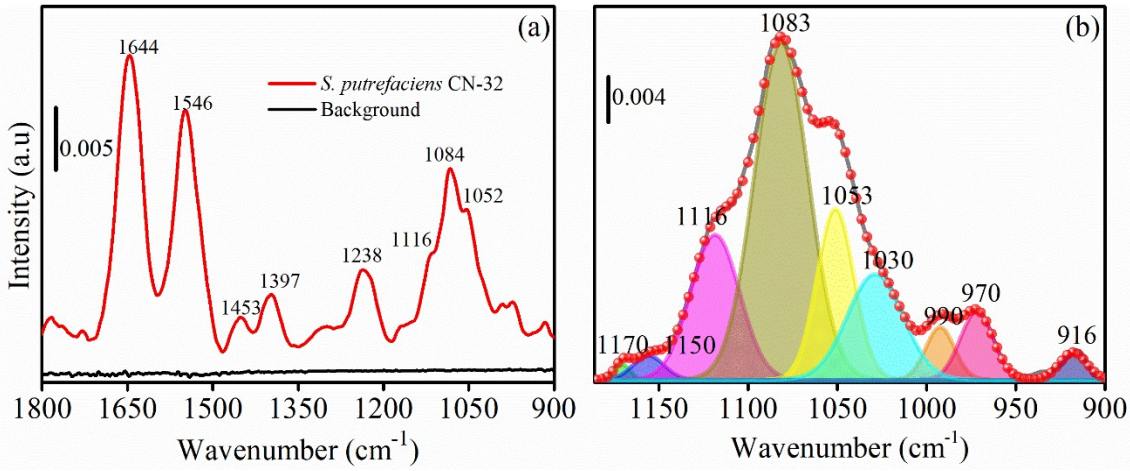

Figure S6. ATR-FTIR spectra of aqueous *S. putrefaciens* CN-32 at pH 6.8. Spectra were collected with a cell density of 10^8 cells mL^{-1}. Each peak position and corresponding functional groups of aqueous *S. putrefaciens* CN-32 are summarized in Table S1.

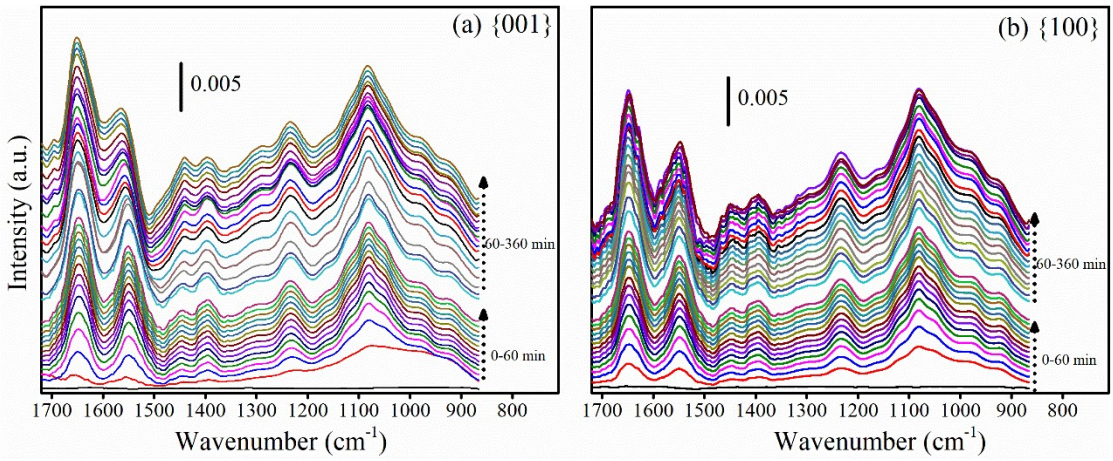

Figure S7. Temporal changes of ATR-FTIR spectra for *S. putrefaciens* CN-32 adhesion on hematite (a) {001} and (b) {100}.

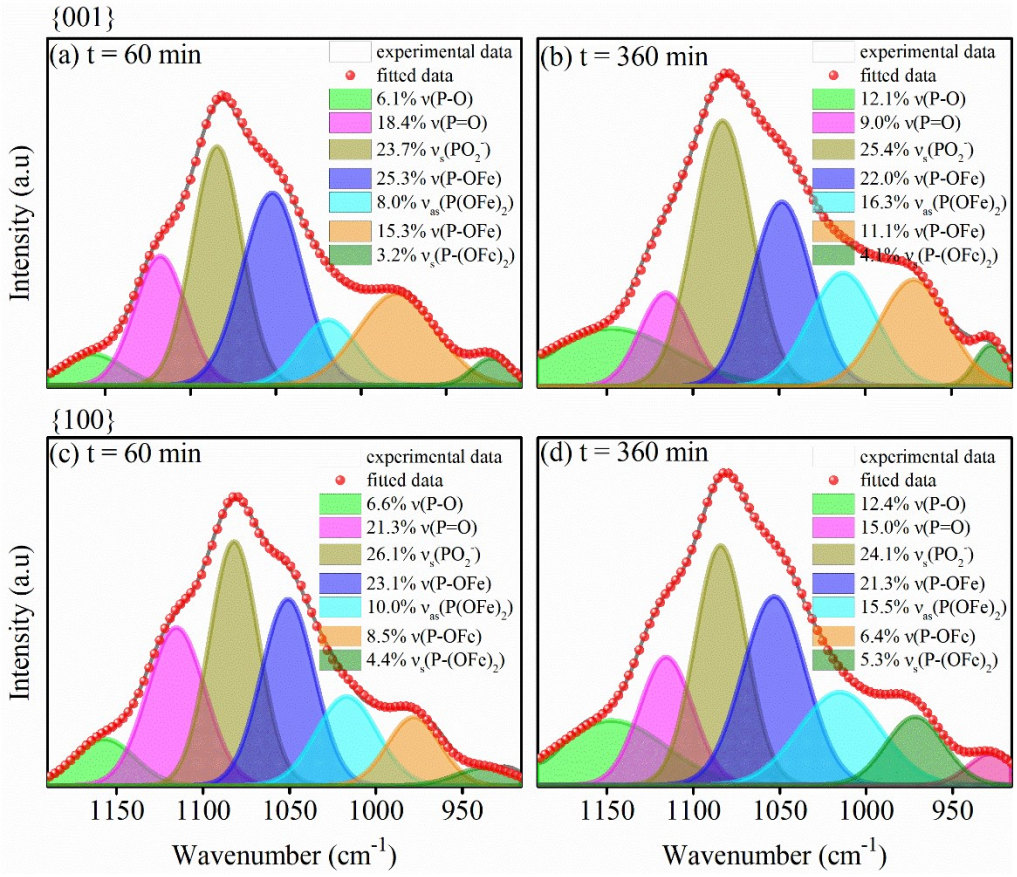

Figure S8. Peak fitting results of ATR-FTIR spectra at 60 min and 360 min during the adsorption process. Hematite (a, b) {001}, and (c, d) {100}. Numbers in each panel represent the percentage of deconvoluted phosphorous functional groups.

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