

ELECTRONIC SUPPLEMENTARY INFORMATION FOR

Nanostructured δ -FeOOH: a novel photocatalyst for water splitting

Márcio César Pereira,^{*,a} Eric Marsalha Garcia^b, Adilson Cândido da Silva^b, Eudes Lorençon^b, José Domingos Ardisson^c, Enver Murad^b, José Domingos Fabris^d, Teodorico de Castro Ramalho^e, Marcus Vinícius J. Rocha^e

^aInstituto de Ciência e Tecnologia, Universidade Federal dos Vales do Jequitinhonha e Mucuri, 39803-371 Teófilo Otoni, Minas Gerais, Brazil.

^bDepartamento de Química, ICEX, Universidade Federal de Minas Gerais, 31270-901 Belo Horizonte, Minas Gerais, Brazil.

^cCentro de Desenvolvimento da Tecnologia Nuclear, 31270-901 Belo Horizonte, Minas Gerais, Brazil.

^dUniversidade Federal dos Vales do Jequitinhonha e Mucuri, 39100-000 Diamantina, Minas Gerais, Brazil.

^eDepartamento de Química, Universidade Federal de Lavras, 37200-000 Lavras, Minas Gerais, Brazil.

*To whom correspondence should be addressed. mcpqui@yahoo.com.br

MATERIALS AND METHODS

Synthesis of δ -FeOOH

The synthesis was carried out using analytically pure chemicals and doubly distilled water. Because of strong foaming in the course of Fe^{2+} oxidation with H_2O_2 , the sample was prepared in a specially designed glass reactor. Basically, 200 mL of a solution containing 5.5604 g of $\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ were mixed with 200 mL of a 2 M NaOH solution. A green precipitated (green rust) was formed. Immediately, 5 mL of H_2O_2 30% were added under stirring. The precipitate turns reddish brown within a few seconds, indicating formation of δ -FeOOH.

Characterization of δ -FeOOH

Transmission electron microscopy (TEM) images were taken with a JEOL JEM 2000EXII transmission electron microscope.

Powder X-ray diffraction (XRD) was carried out using Cu-K α radiation with a Rigaku Geigerflex diffractometer equipped with a graphite diffracted-beam monochromator. Data were collected from 20-70° 2 θ at a step width of 0.5°, 10 s per step. Silicon was used as an external standard.

Mössbauer spectra were collected in a constant acceleration transmission mode with a ~20 mCi $^{57}\text{Co}/\text{Rh}$ source. A spectrometer equipped with a transducer (CMTE model MA250) controlled by a linear function driving unit (CMTE model MR351) was used to obtain the spectra at 20 K. Data were stored in a 1024 channel-MCS memory unit, with the Doppler velocity ranging between about $\pm 12 \text{ mm s}^{-1}$, calibrated with a metallic iron (α -Fe) foil as absorber. The absorbers were prepared with a uniform thickness of 10 mg Fe cm^{-2} , admixing sucrose to the samples. The experimental data were fitted by Lorentzian functions with the least-square procedure of the NORMOSTM-90 computer program.

Surface area was determined by the BET method using N₂ adsorption/desorption in an Autosorb 1 Quantachrome instrument.

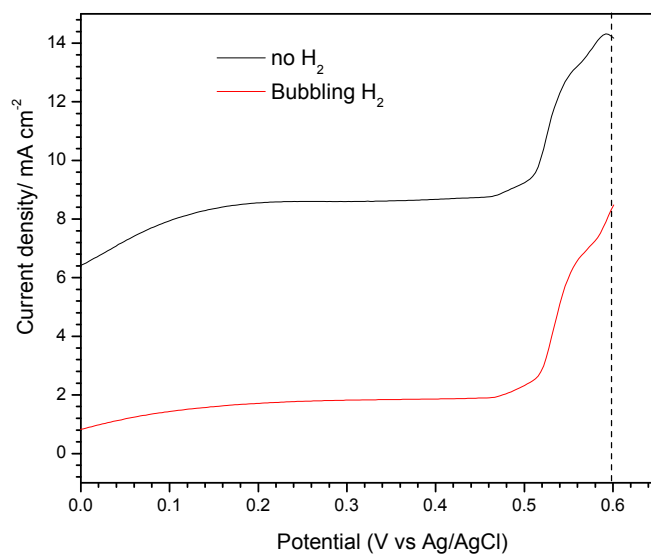
Diffuse reflectance spectra were taken on dry and ground powders using a Varian Cary 5 spectrophotometer equipped with a diffuse reflectance accessory.

Theoretical Calculations

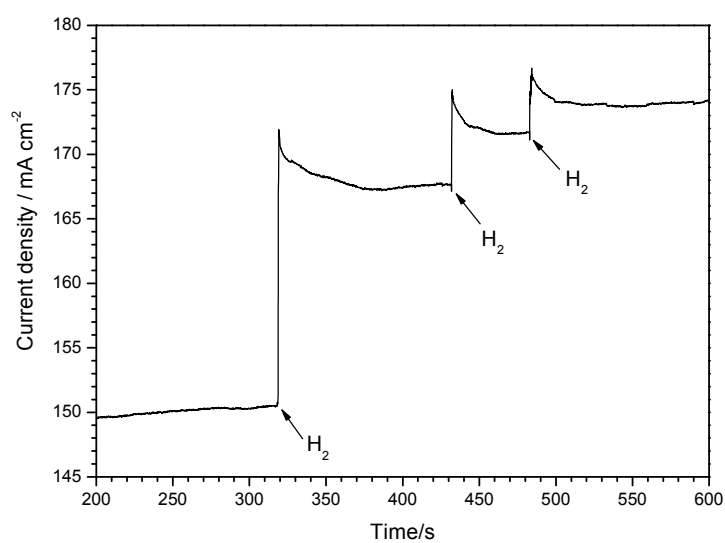
All calculations performed in this study have been made using the Amsterdam Density Functional code for the periodic structures (ADF-Band). This program calculates the electronic structure for periodic systems in one, two, or three dimensions within density functional theory. The electron wave functions are developed on a basis set of numerical atomic orbitals (NAOs) and of Slater type orbitals (STOs). To reduce the size of the basis set, a frozen core approximation was used for the atom cores. A characteristic of this program is that it performs numerical integrations for all the matrix elements. The accuracy of the integration in real space and the sampling of the Brillouin zone for the integration accuracy in k-space are the two major numerical parameters in the calculation. The optimized geometries were evaluated by periodic density functional theory calculations employing generalized gradient (GGA) corrections self-consistently included through the Perdew-Becke-Ernzerhof (PBE) formula. A triple-z Slater-type basis set was used for Fe, O and H atoms. The inner cores of Fe (1s2s2p3s3p) and O (1s) atoms were treated by the frozen-core approximation.

H₂ production measurements

Current measurements were performed by chronoamperometric measurements under a 15 W $\lambda < 300$ nm UV lamp. The produced H₂ was monitored by further oxidation at 0.6 V applied potential. A three-electrode configuration with 1 M NaOH (pH 13.6) as electrolyte using Ag/AgCl in saturated KCl as a reference electrode and 1 mg/mL δ -FeOOH/NaOH solution was used.



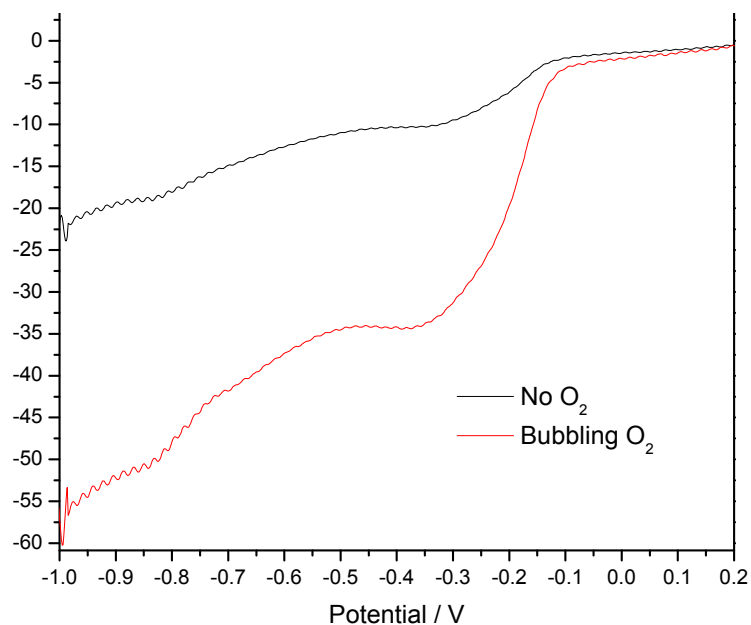
Cyclic Voltammetry of water before and after bubbling H₂.



Current density increases when H₂ is bubbled in water solution.

In order to evaluate the sunlight absorption capacity by δ -FeOOH, an electrochemical cell containing 10 mL of 1 M NaOH solution and 10 mg of dispersed δ -FeOOH was illuminated with sunlight with an intensity (measured with a luximeter) of 2.6 W m⁻². Current measurements were performed by chronoamperometric measurements.

O₂ evolution was followed by chronoamperometric measurements. Typically, an electrochemical cell containing 10 mL of 1 M NaOH solution and 10 mg of dispersed δ-FeOOH was illuminated with sunlight and the produced O₂ was reduced by applying a potential of -0.3 V.



Cyclic voltammetry of water before and after to bubble O₂.

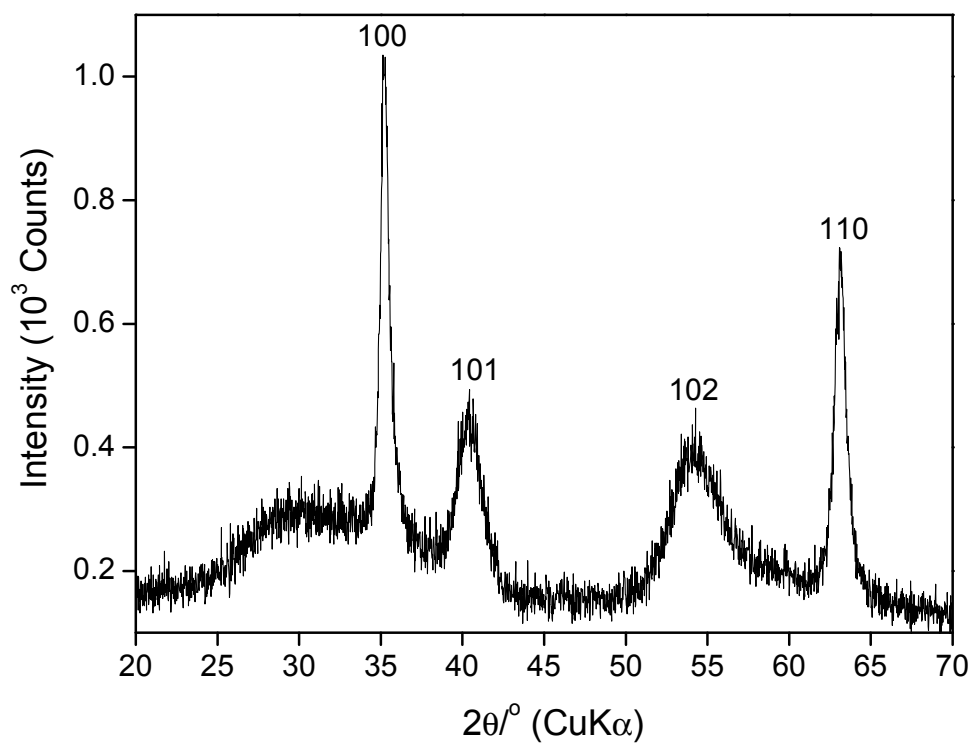


Fig. S1. Powder X ray diffraction pattern of our δ -FeOOH sample.

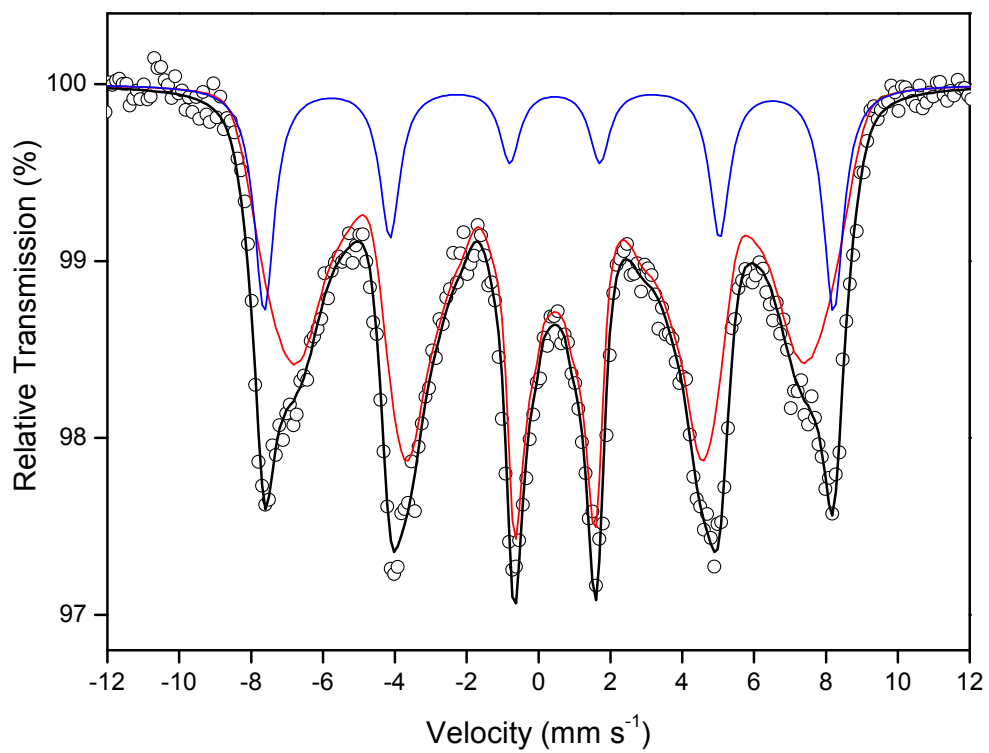


Fig. S2. Mössbauer spectrum of δ -FeOOH at 20 K.

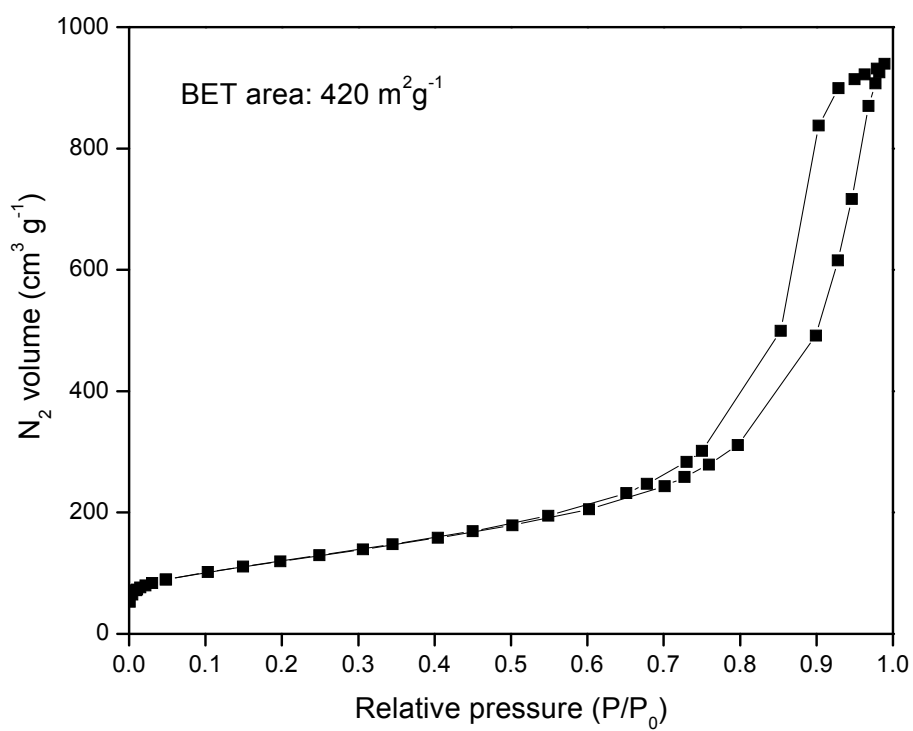


Fig. S3. N₂ adsorption-desorption isotherm.

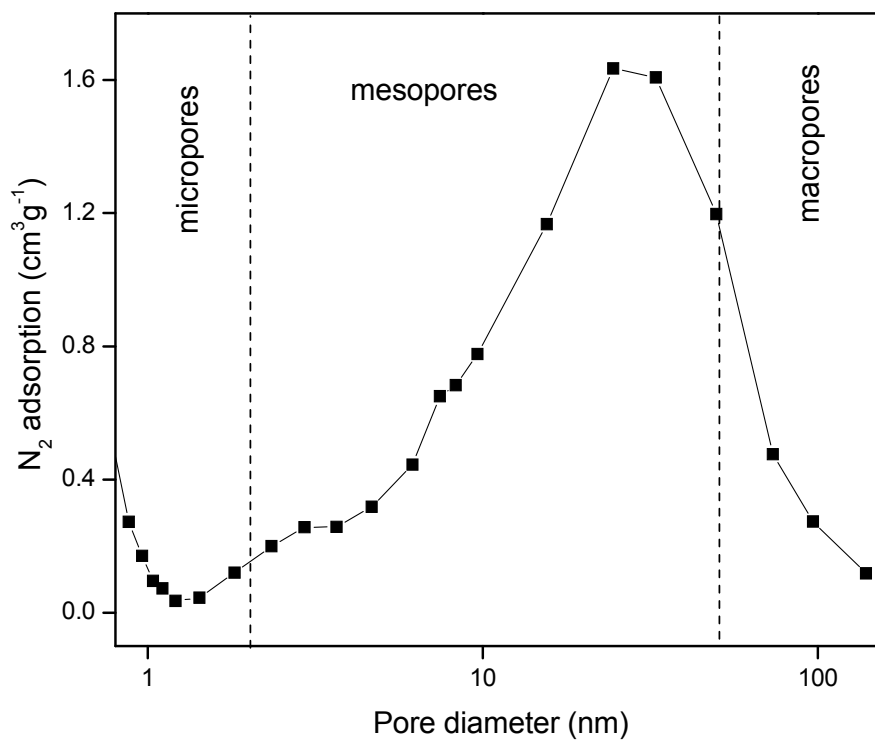


Fig. S4. Pore size distribution using the BJH method.

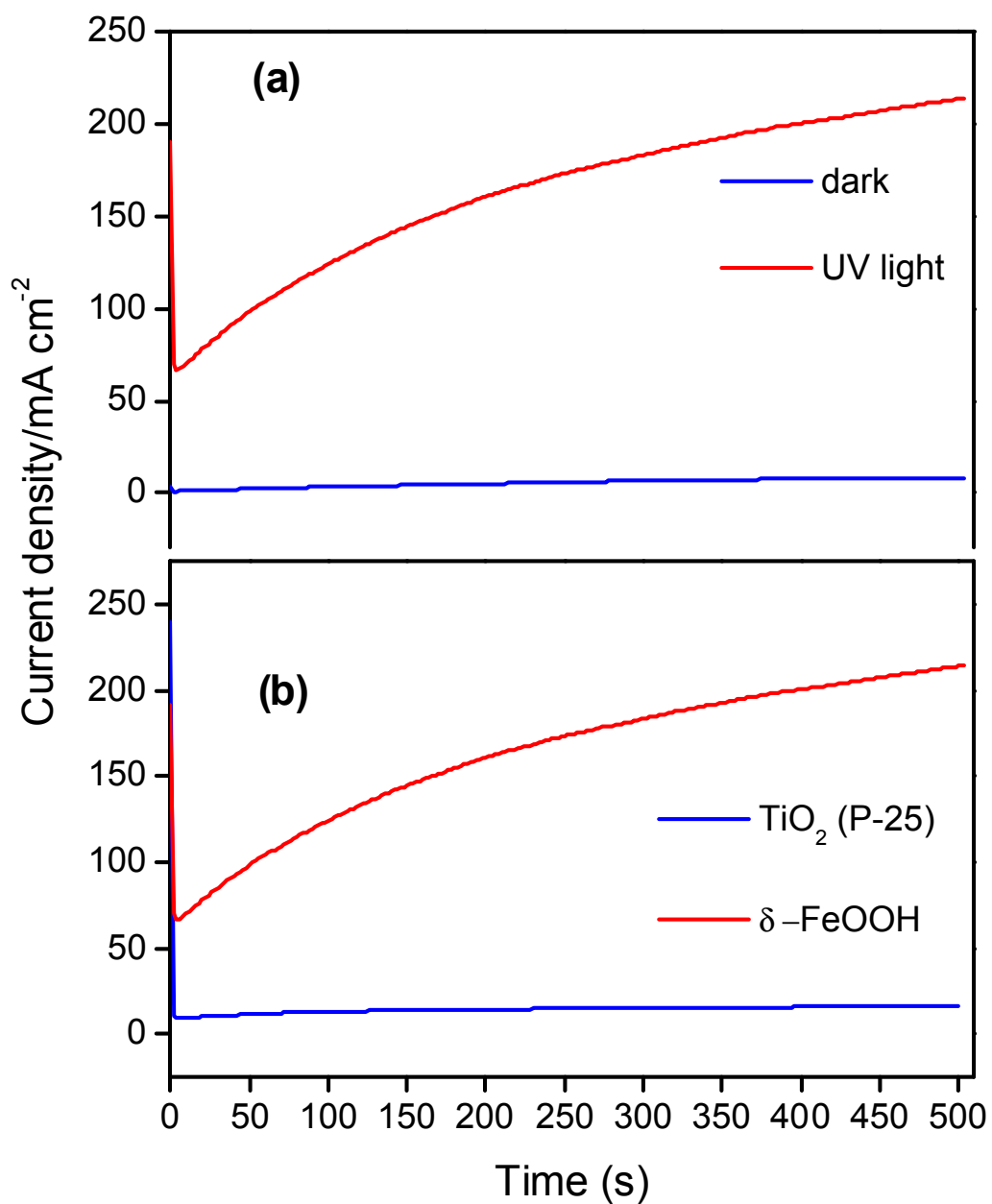


Fig. S5. (a) Current-voltage curves measured in the dark and under a 15 W UV lamp.
(b) Current densities as a function of time using TiO₂ (P-25, Degussa) and δ-FeOOH as photocatalysts.

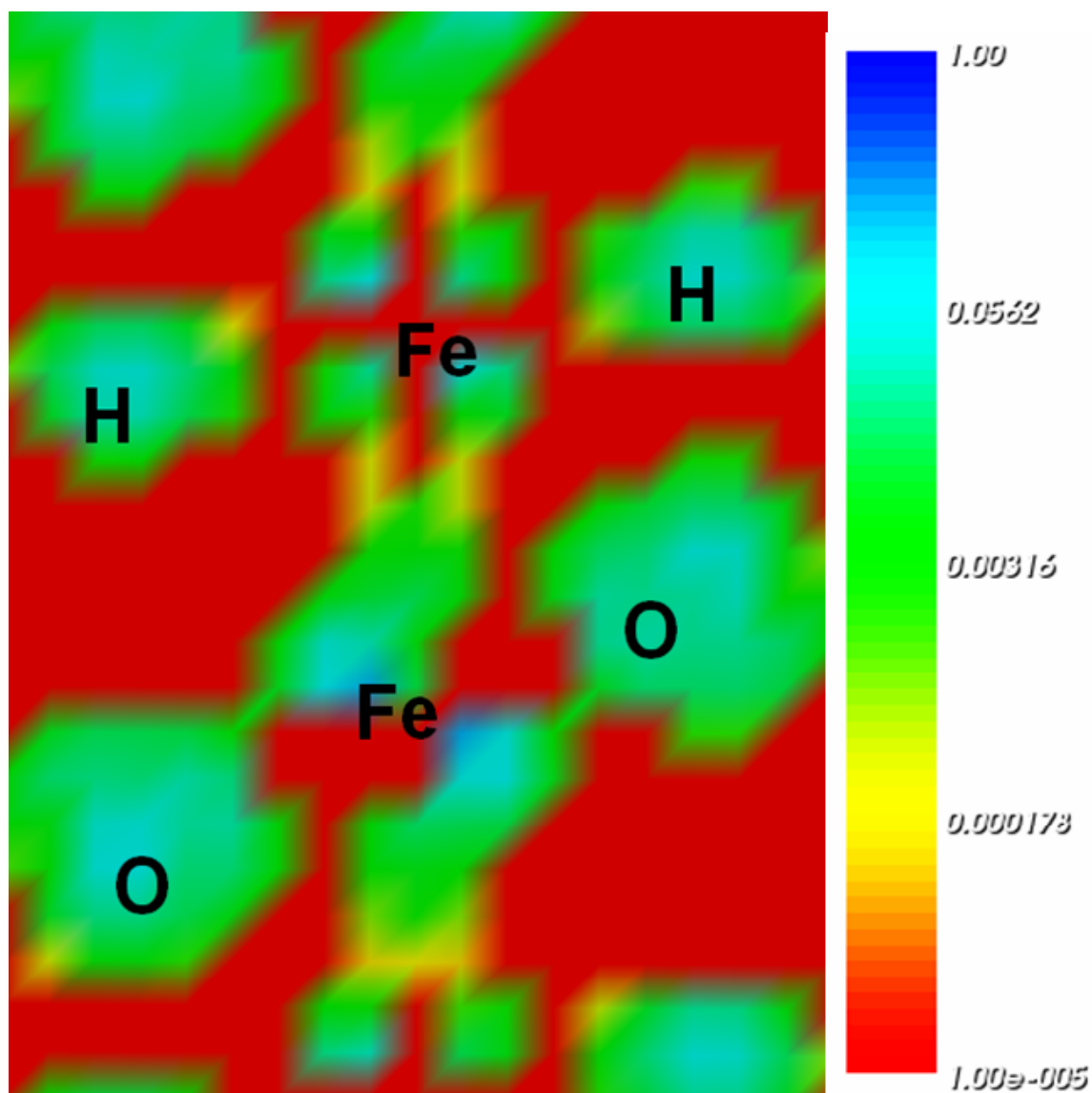


Fig. S6. Charge density contours of our δ -FeOOH sample.