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Yuchao Zhang, Hongna Zhang, Anan Liu, Chuncheng Chen, Wenjing Song, and Jincai Zhao J. Am. Chem. Soc., Just Accepted Manuscript • DOI: 10.1021/jacs.7b10979 • Publication Date (Web): 18 Feb 2018 Downloaded from http://pubs.acs.org on February 18, 2018

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# **Rate-limiting O-O Bond Formation Pathways for Water Oxidation on Hematite Photoanode**

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**ABSTRACT**: Photoelectrochemical (PEC) water oxidation has attracted heightened interest in solar fuel production. It is well accepted that water oxidation on hematite is mediated by surface trapped holes, characterized to be the high valent -Fe=O species. However, the mechanism of the subsequent rate-limiting O–O bond formation step is still a missing piece. Herein we investigate the reaction order of interfacial hole transfer by rate law analysis based on electrochemical impedance spectroscopy (EIS) measurement and probe the reaction intermediates by operando Fourier-transform infrared (FT-IR) spectroscopy. Distinct reaction orders of ~ 1 and ~ 2 were observed in near-neutral and highly alkaline environments, respectively. The unity rate law in near-neutral pH regions suggests a mechanism of water nucleophilic attack (WNA) to -Fe=O to form the O–O bond. Operando observation of a surface superoxide species that hydrogen-bonded to the adjacent hydroxyl group by FT-IR further confirmed this pathway. In highly alkaline

regions, coupling of adjacent surface trapped holes (I2M) becomes the dominant mechanism. While both are operable at intermediate pHs, mechanism switch from I2M to WNA induced by local pH decrease was observed at high photocurrent level. Our results highlight the significant impact of surface protonation on O–O bond formation pathways and oxygen evolution kinetics on hematite surfaces.

#### **INTRODUCTION**

Water oxidation reaction is a crucial module in natural and artificial photosynthetic systems.<sup>1-2</sup> In the overall four-hole and four-proton reaction,<sup>3-5</sup> O–O bond formation is generally the ratedetermining step (RDS), which is associated with high activation barrier as indicated by both kinetic studies and theoretical calculations.<sup>6-25</sup> Mechanisms proposed for O–O bond formation in transition metal complex based catalysts include nucleophilic attack of water/OH<sup>–</sup> to a metal-oxo species (WNA),<sup>8, 13, 26</sup> coupling of two metal-oxo or oxyl radical species (I2M),<sup>13, 18, 26</sup> and insertion of one external oxygen to the oxygen atom between two metal sites.<sup>27-28</sup> The operating pathway is highly sensitive to the electronic structure, primary/secondary coordination sphere and the architecture of catalysts, as well as the reaction conditions.

Solar water splitting based on hematite photoanode has attracted extensive research interest for in-depth understanding of its bulk and surface properties that govern the carrier transport.<sup>5, 29-31</sup> It is widely accepted that water oxidation on hematite is mediated by trapping of photogenerated hole at surface followed by interfacial hole transfer to the adsorbed H<sub>2</sub>O/OH<sup>-</sup>.<sup>5, 22, 30, 32-33</sup> Recently, the long-proposed  $-Fe^{IV}=O$  species, which is generated by hole trapping on hematite surface (–  $Fe^{III}OH + h^+ \rightarrow -Fe^{IV}=O + H^+$ ), has been structurally assigned by operando attenuated total

reflectance infrared spectroscopy (ATR-IR) measurement.<sup>23</sup> By analyzing the dependency on photocurrent and hole density, the involvement of multiple surface trapped holes was suggested in the formation of water oxidation intermediates.<sup>22</sup> In our previous study, it has been established that the interfacial hole transfer step is accompanied by the simultaneous cleavage of O–H bond (of water molecular), i.e., a concerted proton-electron transfer (CPET) process exhibiting pronounced H/D kinetic isotope effect; the kinetic behavior changes at higher pH where proton transfer is not involved in the RDS in this region.<sup>5</sup> In contrast to the intensive investigations to understand the carrier transfer property of hematite, O–O formation mechanism at the hematite/water interface has yet to be demonstrated.

Herein, we revealed distinct O–O bond formation pathways that operate in different pH regions by analyzing the surface hole reaction order and the operando spectroscopic identification of water oxidation intermediates. A first-order dependency of photocurrent with the density of surface trapped holes was demonstrated for PEC water oxidation on the hematite surface under near-neutral condition (pH 10.0). Furthermore, operando PEC ATR-IR measurements identified a surface superoxide species that hydrogen-bonded to adjacent hydroxyl group by its stretching vibration at 1100 cm<sup>-1</sup> with pHs ranging from 8 to 10. <sup>18</sup>O and D isotope labelling experiments further confirmed the nature of the intermediate. Taken together, the O–O bond formation pathway under near-neutral conditions can be described by WNA, followed by another hole transfer to produce surface superoxide species (Scheme 1a). In highly alkaline environment (pH 13.6), the reaction order of surface trapped holes was approximately 2 with faster water oxidation kinetics, suggesting the coupling of the neighboring metal-oxo species (I2M) prevails in the formation of O–O bond (Scheme 1b). In addition, no peroxide or superoxide were observed from PEC ATR-IR measurements above pH 11. In the intermediate pH

region, it is inferred that both mechanisms are operable, and the local pH decrease during water oxidation would change the relative contribution of the two. Our results suggested a surface protonation-status-induced mechanistic switch for the O–O bond formation on hematite surfaces. **Scheme 1.** (a) WNA and (b) I2M mechanisms for the O–O bond formation on hematite surfaces.



#### **RESULTS AND DISCUSSION**

The reaction orders of surface trapped holes were determined at pH 10.0 and 13.6, representing the near-neutral and highly alkaline regions with distinct hole transfer features (CPET and ET), where molecular water and hydroxyl ion act as the dominant hole acceptor,

respectively.<sup>5</sup> The applied potential in this test was 1.23  $V_{RHE}$  to ensure efficient charge separation and therefore the photocurrent was limited by the surface reaction (interfacial hole transfer).<sup>22</sup> Under steady-state illumination (470 nm), the density of surface trapped holes was modulated by the light intensity and calculated according to the method shown in Supporting Information (Figures S1 – S4). It is noted that pH 10.0 is used as the photocurrent density levels at 1.23 V<sub>RHE</sub> (20.0 – 31.5  $\mu$ A cm<sup>-2</sup>) guaranteed a valid fit and simulation of the EIS data for calculating surface hole density ([hole]). The dependency of photocurrent density (J) was fitted to eq 1, where k<sub>wo</sub> is the water oxidation rate constant, and  $\beta$  is the reaction order of surface trapped holes.

$$J = k_{WO} [hole]^{\beta} \tag{1a}$$

$$Log J = \beta log([hole]) + log k_{WO}$$
(1b)



**Figure 1.** Relationship of photocurrent densities ( $\mu$ A/cm<sup>2</sup>) and surface hole densities (number of hole/nm<sup>2</sup>) at (A) pH 10.0 (black square) and pH 13.6 (red dot) and (B) pH 11.5 (black square),

together with the fitting results, under 470 nm illumination in 0.5 M NaClO<sub>4</sub> with the applied potential of  $1.23 V_{RHE}$ .

As shown in the log J- log [hole] profile (Figure 1A), distinct reaction orders, 1.1 and 2.4, were observed at pH 10.0 and 13.6, respectively. The reaction order of 1.1 at pH 10.0 suggested the participation of a single surface trapped hole in the RDS, via nucleophilic attack of water molecule to form the O-O bond (WNA mechanism). According to our early study, the formation of O-O bond via WNA and cleavage of the water O-H bond occurs in a single kinetic step (Scheme 1a, the step labeled RDS).<sup>5</sup> This pathway prevails in near-neutral pH region of 8 - 10, where molecular water is the dominant hole acceptor and the deprotonation agent. In addition, the introduction of 0.05 M borate act as buffer to maintain the local pH at the near vicinity of the surface during EIS measurements showed a similar reaction order of 1.4 (Figure S3), which further supports the WNA mechanism as the dominant pathway for O–O bond formation in this pH region. In contrast, at pH 13.6, the reaction order was calculated to be 2.4, indicating that the rate-limiting formation of O–O bond occurred by the coupling of two neighboring surface trapped holes (I2M mechanism, Scheme 1b), corresponding to oxidation of surface and bulk OH<sup>-</sup> in the highly alkaline environment.<sup>5, 34</sup> While the one-hole transfer pathway is easy to be realized, the multi-hole transfer is difficult to achieve, which requires the presence of adjacent surface trapped holes.<sup>22</sup> In this work, similar surface hole densities were observed in near-neutral and highly alkaline environments. The distinct reaction orders could originate from surface protonation status/hydrogen bond environment that favors different O-O formation pathways.<sup>5, 22</sup>

In the intermediate region, there is insufficient  $OH^-$  in the bulk to compensate  $OH^-$  depletion/proton accumulation at the vicinity of the surface, which has been shown to change water oxidation mechanism on hematite surface.<sup>5, 34</sup> The hole reaction order in this region was

studied at pH 11.5. As shown in Figure 1B, different from the linear-dependence shown in Figure 1A, a non-linear curve was obtained, with the slope of 2.4 at low photocurrent densities which decreased to 0.9 at high photocurrent densities, pointing to a mechanism transition from I2M to WNA. Detailed discussions on local pH and its impact on the operating mechanism can be found in the Supporting Information.

To further identify the O–O bond formation mechanism, the surface species generated during PEC water oxidation were probed by operando PEC FT-IR measurement on hematite photoanode. In a home-made ATR-IR PEC cell (Figure S5), FT-IR spectra were obtained between  $0.6 - 1.6 V_{RHE}$  on a hematite photoanode under AM 1.5 G irradiation in unbuffered pH 8 electrolyte (Figure 2A and Figure S6). The corresponding photocurrent data were collected during the FT-IR measurement as shown in Figure 2B. The onset potential for PEC water oxidation was above 1.2  $V_{RHE}$ ; the photocurrent between 0.6 and 1.2  $V_{RHE}$  (Figure 2B) was attributed to surface hole trapping process.<sup>5, 32-33</sup> Within this potential range, the spectra did not exhibit notable changes except for some fluctuation around 1100 cm<sup>-1</sup>. As water oxidation current took off at 1.3 V<sub>RHE</sub>, the signal of weakly surface-adsorbed water (2800 - 3200 cm<sup>-1</sup>), Figure S7) decreased and a new band centered at c.a. 1100 cm<sup>-1</sup> emerged (Figure 2A). The potential dependency of intensities of the new band were similar as photocurrent (Figure 2B), suggesting that the new species generated above  $1.2 V_{RHE}$  is a water oxidation intermediate. The FT-IR absorption around 800 cm<sup>-1</sup> also increased but was too obscure for quantification (Figure S8).



**Figure 2.** (A) FT-IR spectra on the hematite photoanode under AM 1.5 G illumination in unbuffered pH 8 electrolyte (0.5 M NaClO<sub>4</sub>) with applied potentials from 0.6  $V_{RHE}$  to 1.6  $V_{RHE}$ . (B) Steady-state photocurrent density ( $\mu$ A/cm<sup>2</sup>) and the area of the IR band at 1100 cm<sup>-1</sup> as a function of applied potentials.

The new vibrational band at 1100 cm<sup>-1</sup> observed under PEC water oxidation lies in the range reported for stretching vibration of superoxide species  $(1200 - 1070 \text{ cm}^{-1})$ .<sup>16</sup> To confirm the chemical nature of the evolved species under water oxidation, FT-IR measurements were performed in <sup>18</sup>O- or D-labelled water. In H<sub>2</sub><sup>18</sup>O, the isotope counterparts of the 1100 cm<sup>-1</sup> species emerged at 1082 cm<sup>-1</sup> (Figure 3). The ~ 18 cm<sup>-1</sup> shift is expected for the partially labelled superoxo stretching mode, produced by the reaction of  $-\text{Fe}=^{16}\text{O}$  with H<sub>2</sub><sup>18</sup>O. No <sup>18</sup>O<sup>18</sup>O species (~ 44 - 61 cm<sup>-1</sup> shift to lower wavenumber) was resolved. The absence of fully labeled product could result from the slow exchange of surface adsorbed H<sub>2</sub><sup>16</sup>O/<sup>16</sup>OH<sup>-</sup> with H<sub>2</sub><sup>18</sup>O. On the other hand, the ATR-IR PEC cell is open to the air and the diffusion of H<sub>2</sub><sup>16</sup>O from the air to the solution cannot be avoided. In D<sub>2</sub>O, the 47 cm<sup>-1</sup> shift to lower wavenumber (Figure 3) indicates the interaction of the intermediates with proton. These results suggest that the observed

intermediate during PEC water oxidation is a surface superoxide species that hydrogen-bonded to the adjacent surface hydroxyl group (Scheme 1a). Such structure, rather than a dangling hydrogenated superoxo, is proposed considering that the proton-coupled electron transfer (PCET) removes one electron and one proton from surface-bonded –OOH group to form superoxide, where an adjacent –OH group contributes to the hydrogen bond (Scheme 1a). The hydrogen bond bridged structure causes a redshift of IR absorption peak compared with the dangling structure,<sup>16</sup> which probably accounts for that the stretching vibration (1100 cm<sup>-1</sup>) lies at the lower limit of the reported values for superoxide species (1200 – 1070 cm<sup>-1</sup>). Although the bending vibration of surface hydroperoxide also possesses IR band in the range of 1250 – 1120 cm<sup>-1</sup>, the significantly smaller isotope shift observed here (47 cm<sup>-1</sup> vs. 350 – 220 cm<sup>-1</sup> for bending vibration of hydroperoxide in D<sub>2</sub>O) excludes such assignment.<sup>35</sup> Based on the reaction order of ~1 under near-neutral pH condition and the observed superoxide intermediate, we conclude that the hydrogen-bonded superox species is produced via the rate-limiting nucleophilic attack and the following hole transfer process (Scheme 1a).



**Figure 3.** FT-IR spectra recorded under AM 1.5 G illumination in unbuffered H<sub>2</sub>O, D<sub>2</sub>O and H<sub>2</sub><sup>18</sup>O electrolytes (0.5 M NaClO<sub>4</sub>) with applied potential of 1.6 V<sub>RHE</sub> at pH 8.

The band at 1100 cm<sup>-1</sup> was most prominent at pH 8, and was also observed in the presence of 0.1 M phosphate buffer at pH 8 (Figure S9). With increase in pH, its intensity gradually decreased and completely disappeared at pH 11 (Figure 4, spectra obtained under photoelectrolysis at 1.6  $V_{RHE}$ ). The pH dependency of the IR absorption suggested that the observed hydrogen-bonded superoxide only accumulated at lower pH conditions, where the surface interfacial hole transfer process occurs via the slow WNA mechanism (Scheme 1a). As the O–O bond formation is well accepted as the RDS for water oxidation, in this mechanism only

one hole is required before the RDS is accomplished, which is consistent with the observed near unity rate law in near-neutral pH region. The reaction order of 2.4 at pH 13.6 indicates of the presence of adjacent surface trapped holes that are accumulated before or within the RDS. Rapid coupling of surface trapped holes gives geometric symmetric O–O structure that is IR silent, or the intermediate is short-lived thereby is not probably detected by our apparatus. The opposite pH dependency of photocurrent and the 1100 cm<sup>-1</sup> band intensity (Figure S10) also agrees with the rate law analysis results, confirming that distinct O–O formation pathways dominants in near-neutral and highly alkaline environments, respectively, while both contribute to oxygen evolution in the intermediate pH values.



**Figure 4.** FT-IR spectra recorded on the hematite photoanode under AM 1.5 G illumination with applied potential of  $1.6 V_{RHE}$  at different pHs.

Previous transient absorption spectroscopic research revealed the independency of time scales of water oxidation reaction with the concentration of photogenerated holes in alkaline region (0.1M NaOH electrolyte, pH  $\sim$ 12.8), which suggested a single-hole oxidation mechanism.<sup>36-37</sup> Recently, the photoinduced absorption measurements suggested the involvement of multi-hole

transfer pathway on the hematite surface under high intensity irradiation; the authors proposed that both the coupling of surface trapped holes and the nucleophilic attack of OH<sup>-</sup> to a bridging oxygen are plausible.<sup>22</sup> Theoretical calculation suggested that WNA and I2M mechanisms on hematite surface are similar in free energy change and are kinetically competitive.<sup>38</sup> Here the switch of O–O bond formation pathway from near-neutral to highly alkaline conditions can originate from the different surface organization of water and hydroxyl group (pK<sub>a</sub> of hematite (001) facet is c.a. 10).<sup>5, 39</sup> An implication from our results is that the water oxidation kinetic and formation mechanism of O–O bond can be tuned by changing the local environment (e.g., surface vacancy density or introducing heteroatoms) at the interface. It should be noted that on our hematite nanowire photoanode, spectroscopic feature of –Fe<sup>IV</sup>=O that exhibited IR signal at 898 cm<sup>-1</sup> <sup>23</sup> or UV-vis absorption at 570 nm <sup>21</sup> was not resolved. The different surface architectures or active sites of hematite nanowires from the ALD-prepared samples<sup>23, 32-33</sup> may changes the kinetics of the associated elemental steps and the metastable intermediates.<sup>40-41</sup>

#### CONCLUSION

In conclusion, a unity rate law for surface trapped holes suggests nucleophilic attack of water to surface trapped holes to construct the O–O bond in near-neutral pH region where molecular water is the dominant hole acceptor. Operando ATR-IR characterization of hematite photoanode under PEC water oxidation conditions further revealed a hydrogen-bonded surface superoxide species produced via WNA and the following non-rate-limiting hole transfer step. Partially surface deprotonation at increased pHs (10-12) opens up the pathway of coupling of multiple surface  $-Fe^{IV}=O$  species for the O–O bond formation, showing faster water oxidation kinetics without accumulation of stable intermediates. WNA in this region are also operable but its contribution decreases with pH. At high pH extreme ( $\geq$ 13), the I2M mechanism prevails. Our

study establishes the O–O bond formation mechanism in PEC water oxidation on hematite photoanodes and demonstrates the sensitivity of reaction pathways to the interfacial environments.

# **EXPERIMENTAL SECTION**

**Photoanode preparation** Hematite nanowires were fabricated on a fluorine-doped tin oxide (FTO, TCO-15, Nippon Sheet Glass, Japan, 14 ohm/sq) glass substrate by hydrothermal procedure.<sup>42</sup> Briefly, 100 ml aqueous solution mixed with 2.43 g of ferric chloride (FeCl<sub>3</sub>.6H<sub>2</sub>O, Alfa Aesar, 98%) and 0.85 g of sodium nitrate (NaNO<sub>3</sub>, J&K, 99%) was adjusted to pH 1.4 by HCl in a Teflon-lined stainless-steel autoclave. Several FTO glass slides ( $2 \times 4$  cm for ordinary PEC experiments and  $0.2 \times 4$  cm for ATR-IR measurements) were first washed with acetone, ethanol, and deionized water, and then placed in the autoclave and heated at 95°C for 4 hours. A uniform layer of iron oxyhydroxides (FeOOH) was fabricated on the FTO glass (with an active area of 4 cm<sup>2</sup> for ordinary PEC experiments and 0.6 cm<sup>2</sup> for ATR-IR measurements), and then was washed completely with deionized water to remove any residual salts. The iron oxyhydroxide film was sintered in air at 550°C for 2 hours and at 750°C for 15 min to convert into hematite.

**Photoelectrochemical characterization** PEC performances of the photoanodes were measured in a three-electrode electrochemical cell. The measured potentials were converted to the RHE scale according to the Nernst equation:  $E_{RHE} = E_{Ag/AgCl} + 0.059pH + 0.1976$ . EIS experiments were measured under 470 nm LED illumination, recorded by an electrochemical workstation (PGSTAT302N autolab, Metrohm). For EIS measurement, a sinusoidal voltage pulse of 10 mV amplitude was applied on a bias potential, with frequencies ranging from 10 kHz to 1Hz. The raw data were fitted and simulated using Nova 1.10 software from Metrohm Inc. The pH values of the solution were measured by a pH-meter (Thermo Scientific, 3-Star). All experiments were performed at room temperature of  $25 \pm 3^{\circ}$ C.

**ATR-IR measurement** Operando PEC ATR-IR measurement was performed by a Thermo Nicolet 6700 FT-IR spectrometer equipped with a mercury cadmium telluride (MCT) detector. With the home-made PEC cell as shown in Figure S5, the hematite photoanode was pressed onto the ZnSe prism. A Au wire was used as the working electrode connection due to its high water-oxidation overpotential. Back-illumination was performed with a 150 W Xenon lamp coupled to a filter (AM 1.5 G) as the light source. An optical fiber was used to guide the AM 1.5 G illumination onto the measured system. The light power density of 100 mW/cm<sup>2</sup> was measured with a radiometer (CEAULIGHT, CEL-NP2000). IR spectra were recorded at different applied potentials for 1 min over the frequency range from 4000 to 650 cm<sup>-1</sup> by averaging 64 scans with a resolution of 4 cm<sup>-1</sup>. For isotope experiments, H<sub>2</sub><sup>18</sup>O (~ 98%) was purchased from Jiangsu-Changshu-Chemical, Ltd. (Changshu, Jiangsu, P.R. China). D<sub>2</sub>O (99.9%) were purchased from Cambridge Isotope Laboratories, Inc. The pD values were calculated followed the relation pD = pH<sub>read</sub> + 0.4. The pD values were adjusted by NaOD (Alfa Aesar, 40% w/w solution in D<sub>2</sub>O, 99.5 % (Isotopic) and D<sub>2</sub>SO<sub>4</sub> (Alfa Aesar, 96% min in D<sub>2</sub>O, 99.5% (Isotopic).

#### ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge via the Internet at http://pubs.acs.org.

Discussions on local pH and mechanism switch with pH. EIS data obtained under the 470 nm illumination with the applied potential of 1.23  $V_{RHE}$  under unbuffered pH 10.0, buffered pH 10.0 (0.05 M borate), unbuffered pH 11.5 and pH 13.6. Model circuit for EIS fit and simulation. FT-IR spectra obtained on the hematite photoanode under AM 1.5 G illumination in unbuffered pH 8 electrolyte (0.5 M NaClO<sub>4</sub>) with applied potentials from 0.6  $V_{RHE}$  to 1.6  $V_{RHE}$ . FT-IR spectra obtained in buffered pH 8 electrolyte (0.1 M phosphate).

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# Notes

The authors declare no competing financial interest.

#### ACKNOWLEDGMENT

This work was supported by NSFC (Nos. 21590811, 21677148, 21521062, 21525729), the "Strategic Priority Research Program" of the Chinese Academy of Sciences (No. XDA09030200) 15

and the "Key Project of Frontier Science" (No. QYZDY-SSW-SLH028) of the Chinese Academy of Sciences. We also express our thanks to Prof. Wei David Wei of University of Florida for his kind support in EIS measurement.

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