Acid Treatment Enables Suppression of Electron-Hole Recombination in Hematite for Photoelectrochemical Water Splitting**

Yi Yang,[a] Mark Forster,[b] Yichuan Ling,[a] Gongming Wang,[a] Teng Zhai,[a],[c] Yexiang Tong,[c] Alexander J. Cowan*,[b] and Yat Li*,[a]

Abstract: *We report a new strategy for efficient suppression of electron-hole recombination in hematite photoanodes. Acid-treated hematite show substantially enhanced photocurrent density compared to untreated samples. Electrochemical impedance spectroscopy studies reveal that the enhanced photocurrent is partly due to improved efficiency of charge separation. Transient absorption spectroscopic studies coupled to electrochemical measurements indicate that in addition to improved bulk electrochemical properties, acid treated hematite has significantly decreased surface electron-hole recombination losses due to a greater yield of the trapped photoelectrons being extracted to the external circuit.*

Hematite has been extensively studied as photoanodes for water splitting.[1-5] Nevertheless, poor hole transfer efficiency and late turn-on characteristics limits their photoelectrochemical (PEC) performance.[6-7] To address these limitations, a number of hematite nanostructures have been developed to minimize hole transfer distance.[1, 8-9] Surface passivation has been found to be another effective method to enhance hole transfer efficiency by reducing the number of surface trap states.[6-7, 10] Likewise, hole transfer efficiency can be improved by decorating hematite surface with oxygen evolution reaction catalysts which can enhance activity either by reducing the over-potential for water oxidation[11-13] or through the suppression of slow recombination due to interfacial electronic effects.[14-16] Previous studies also suggested that the turn-on characteristics of hematite photoanodes may be closely related to their surface nature. [17-18] Jang *et al.* reported a re-growth strategy to reduce surface disorders of hematite and achieved a significantly shifted onset voltage. [17] Yet, the performance of hematite photoanodes can also be limited by the efficiency of initial charge separation and electron transfer, which has been rarely studied. Here we demonstrate that a simple acid treatment method can substantially enhance the efficiency of electrons moving out of traps in hematite nanowire photoanodes, and therefore reduce the electron-hole recombination loss and improve PEC performance.

Hematite nanowires intentionally doped with Sn were synthesized on a FTO glass substrate according to a literature reported method (Method, SI).[9] Nanowires are vertically aligned on the FTO substrate, with average diameter of 100 nm and length of ~1 μm (Fig S1a, SI). The hematite nanowire film was immersed in pure acetic acid solution for 5 min, followed by annealing in air at 450 °C for 30 min. The nanowire morphology and crystal phase remained unchanged upon acid treatment and annealing (Fig S1b and Fig S2, SI). The acid-treated hematite also has an equally smooth surface as the untreated sample with no sign of surface etching or shell coating (Fig S3, SI), as well as comparable surface area (Fig S4, SI). X-ray photoelectron spectroscopy (XPS) was used to investigate the possible influence of acid treatment on the chemical nature of the hematite surface (Fig S5, SI). Both untreated and acid-treated samples exhibit a Fe 2p1/2 peak and a Fe 2p3/2 peak centered at binding energies of 724.5 eV and 711.4 eV, which are typical values reported for Fe^{3+} in Fe_2O_3.[19] Notably, acid-treated hematite has a slightly higher Fe^{2+} signal (a satellite peak located at 716 eV) [20] than untreated sample, suggesting Fe^{2+} sites were created during acid treatment. Acid-treated hematite also exhibits an additional shoulder peak at 531.9 eV that can be attributed to Fe-OH, which has been reported to be located at the binding energy ~1.5-2.0 eV higher than the O 1s peak of Fe_2O_3.[21] The XPS data confirm the increased amount of hydroxyl groups on the hematite surface following acid treatment, resulting in the formation of more Fe^{2+} sites to balance the charge.

Acid-treated hematite showed considerably enhanced photocurrent density compared to that of untreated sample (Fig 1a). To understand the effect of thermal annealing on the performance of hematite we also collected *I-V* curve from the hematite sample without acid treatment but thermally annealed under the same conditions. Untreated but thermally annealed sample exhibits comparable photocurrent densities as untreated sample (Fig S6, SI), indicating that the combination of acid treatment and the subsequent thermal annealing process is essential for the enhanced performance of the acid-treated sample. As expected, the acid-treated hematite also exhibits significantly enhanced incident photon-to-current covnersion efficiency (IPCE) values compared to the untreated sample over the entire wavelength we studied. IPCE values of both samples gradually drop to zero at wavelengths beyond 600 nm, in accordance with the bandgap of hematite. Additionally, there is no obvious change in light absorption capability of hematite upon acid treatment (Fig S7, SI). Taken together, these results proved that the enhanced photocurrent density of acid-treated hematite is due to improved efficiency of charge collection following light harvesting. Additionally, the acid-treated hematite shows excellent photostability (Fig 1b, inset), proving that the enhanced photocurrent is not at the expense of photostability. In addition to acetic acid, we also tested other inorganic acids including HCl, HNO_3 and H_3PO_4 for treating hematite nanowire films. Hematite films treated with different acids all show pronounced enhancement in

[a] Y. Yang, Dr. Y. Ling, Dr. G. Wang, Dr. T. Zhai, Prof. Y. Li
Department of Chemistry and Biochemistry
University of California, Santa Cruz
Santa Cruz CA 95064 (USA)
E-mail: yatli@ucsc.edu
[b] M. Forster, Prof. A. J. Cowan
Department of Chemistry and Stephenson
The University of Liverpool
Liverpool L69 7ZD (UK)
E-mail: A.J.Cowan@liverpool.ac.uk
[c] Dr. T. Zhai, Prof. Y.Tong
School of Chemistry and Chemistry Engineering
Sun Yat-Sen University
Guangzhou 510275, People's Republic of China

photocurrent (Fig S8, SI) proving that acid treatment is a general strategy for enhancing the performance of hematite photoanode.
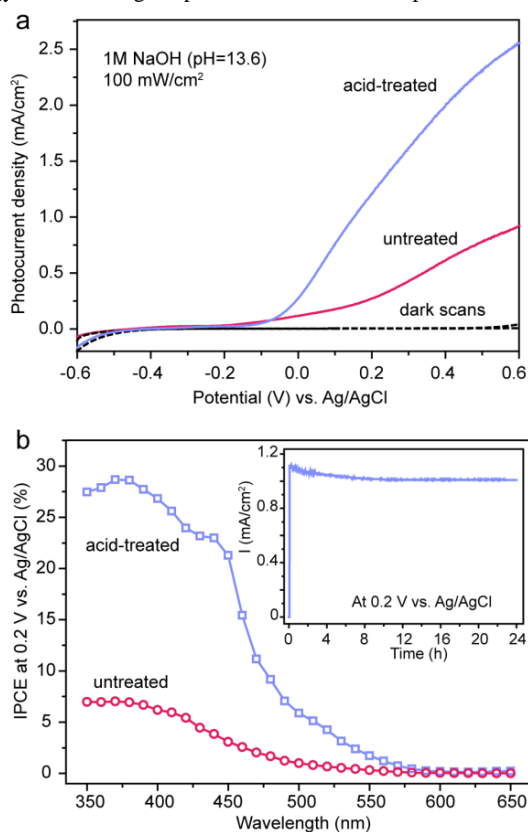

Fig 1. a) I-V curves collected for untreated and acid-treated hematite photoaonodes at 20 mV/s in a 1 M NaOH electrolyte solution under illumination by simulated solar light of 100 mW/cm^2 and in the dark. b) IPCE spectra of untreated and acid-treated hematite. Inset: *I–t* curve of acid-treated hematite.

We investigated the influence of acid treatment on the electronic properties of hematite and its possible relation to the enhanced charge collection efficiency and photoactivity. Fig 2a shows the Mott–Schottky plots generated based on the capacitances derived from the electrochemical impedance values obtained at each potential. The donor density of acid-treated hematite was calculated to be 1.11×10^{20} cm^{-3}, which is an order of magnitude higher than that of the untreated sample (1.06×10^{19} cm^{-3}). Meanwhile the donor density of thermally annealed hematite without acid treatment (1.23×10^{19} cm^{-3}) is very similar to the untreated sample (Fig S9, SI). The increased donor density is expected to improve the electrical conductivity of hematite, and therefore reduce the electrode internal resistance and the voltage drop at the interface of hematite and FTO substrate. Furthermore, electrochemical impedance spectroscopy (EIS) measurements was used to investigate the influence of acid treatment on the charge transfer at the hematite/electrolyte interface. The Nyquist plots of hematite electrodes consist of a semi-circle in the high-frequency domain and a steep line in the low-frequency domain (Fig 2b). Figure 2b inset shows the equivalent circuit used to fit the EIS data. Significantly, the charge transfer resistance (R_{ct}) of hematite was considerably reduced from 113.6 Ω to 5.1 Ω after acid treatment (Table S1, SI). The reduced R_{ct} can be attributed to the improved electrical conductivity of acid-treated hematite.
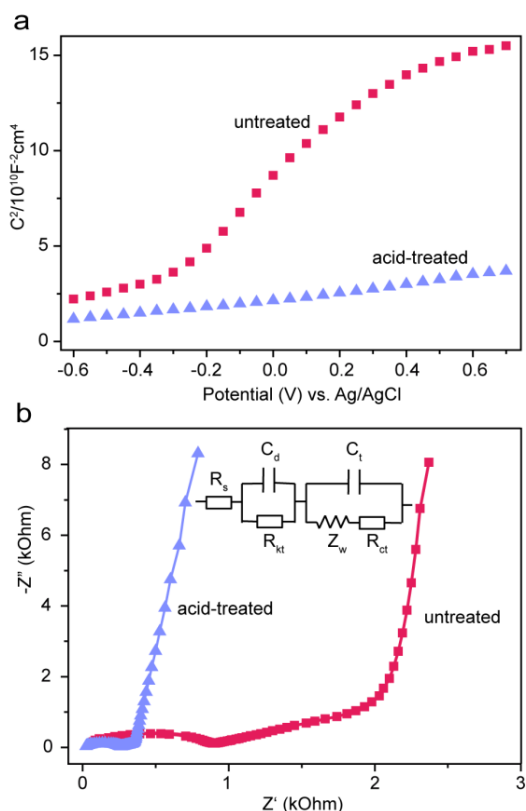

Fig 2. a) Mott-Schottky plots of untreated and acid-treated hematite electrodes collected at 10 kHz in the dark. b) EIS spectra of untreated and acid-treated hematite electrodes. Inset: equivalent circuit used to fit the spectra (Experimental section, SI).

It is anticipated that the acid treatment primarily modifies the surface properties of the hematite electrode, however in-light of the measured increased donor density it is also important to assess if the improved activity can be in part at least related to a difference in the yield of initial charge separation, which is defined as the yield of photogenerated holes reaching the surface. Sivula *et al.* have previously described a simple methodology for distinguishing between bulk and surface electron-hole recombination losses,[22] where the photoelectrochemical response in the presence of H_2O_2, an efficient hole scavenger, is compared to that achieved during water oxidation. Similar experiments here do indicate that we achieve a slight decrease in bulk-electron hole recombination with the yield of photoholes reaching the surface increasing from *ca.* 33% to nearly 50% for acid treated hematite at 0.2 V vs. Ag/AgCl (Fig S10, SI). Whilst significant, this change in charge separation yield alone is not sufficient to explain the very large change in IPCE measured during water splitting, which at 0.2 V vs. Ag/AgCl, 350 nm, increases approximately four-fold (7% to 27%), Fig 1b. This indicates that a change in the surface kinetics is likely to be a more significant factor controlling the enhanced activity.

Transient absorption (TA) spectroscopy and transient photocurrent (TPC) measurements allow the direct measurement of the yield and dynamics of photogenerated charges within a photoelectrode. Previous TA spectroscopic studies of hematite photoelectrodes have examined numerous aspects of the photophysics and chemistry of extrinsically and intrinsically doped hematite, including the role of co-catalysts on hole kinetics, the effect of bias on charge trapping and recombination, and the effect of surface passivation on trap states, from the fs–ms timescale. [9, 23-24] In-line with these past studies the TA

spectra (500-825 nm) of untreated and acid-treated samples, at a potential where water oxidation is expected to occur (0.2 V), show two distinct features which are well documented in the literature for hematite [24-26]; a broad positive transient absorption at wavelengths greater than ~600 nm and a sharp bleach at ~575 nm which are assigned to photoholes and trapped photoelectrons respectively (Fig 3a,b). The similar magnitude of the maximum transient signal at 575 nm (*ca.* -1x10^{-4} O.D. Fig 4), indicates that following initial charge separation a similar yield of photoelectrons are trapped at inter-band states in both films. However we find that the rate of recovery of the 575 nm bleach, i.e. the rate of loss of trapped electrons, is markedly accelerated following the acid treatment and can be well fitted to a single exponential decay function with a time constant of 7 ± 1 ms for the acid treated sample and 40 ± 4 ms for the untreated sample. Trap mediated electron-hole recombination at, or close to the hematite surface has been shown to be a significant loss pathway in several studies [23, 27-29] and here we explore the fate of the de-trapped electrons measured by TA through comparison to the recorded transient photocurrent (Fig 4 and Fig S11, SI). In both samples the rate of decay of the 575 nm TA signal is similar to the rate of charge extraction as measured by TPC (Fig 4b), indicating that a portion of the de-trapped electrons are able to reach the external circuit. However despite the similar initial concentration of trapped electrons, we note a far lower charge extraction yield in the untreated sample (Fig 4b). This indicates that in parallel to electron transport to the external circuit, a 2nd process is occurring which dominates in the untreated sample. We assign the parallel process to recombination, which on this timescale is anticipated to be with surface trapped holes. Here we propose a simple parallel kinetics model where the trapped electrons can either be extracted to the external circuit to give rise to a photocurrent, or be lost through recombination with trapped holes with the two processes having rate constants k_{ext} and k_{rec} respectively (Fig S12, SI). In our kinetics model the overall rate of loss of the trapped electrons is given by the sum of the parallel rate constants and the yield of each pathway is determined by the relative rate constants of the processes, a full kinetic analysis is in the Fig S13 (SI).[30] The greater relative rate constant for the detrapping and charge extraction pathway following acid treatment gives rise to a higher charge extraction yield. TA spectroscopic (Fig S14, SI) and TPC measurements of a hematite film which has undergone thermal annealing without acid treatment show only a slight change in the rate (Fig S15, SI) and yield of charge extracted (Fig 4) when compared to the untreated sample, again confirming that both the acid treatment and the subsequent thermal annealing process are required for improved performance. This indicates that the combined acid and thermal treatments modify either the nature or position of the available trap sites. In this study we are unable to definitively ascertain the spatial positioning of the trap sites within the film however the acid-treatment would be expected to primarily affect surface states. Jang et al., also recently proposed a "re-growth" approach to hematite that modifies surface defects. [17] In addition, Cao et al. reported that the surface trapped electrons are involved in the back reaction for oxygen reduction. [31] The enhanced rate of detrapping photo-electrons can suppress the back reaction.
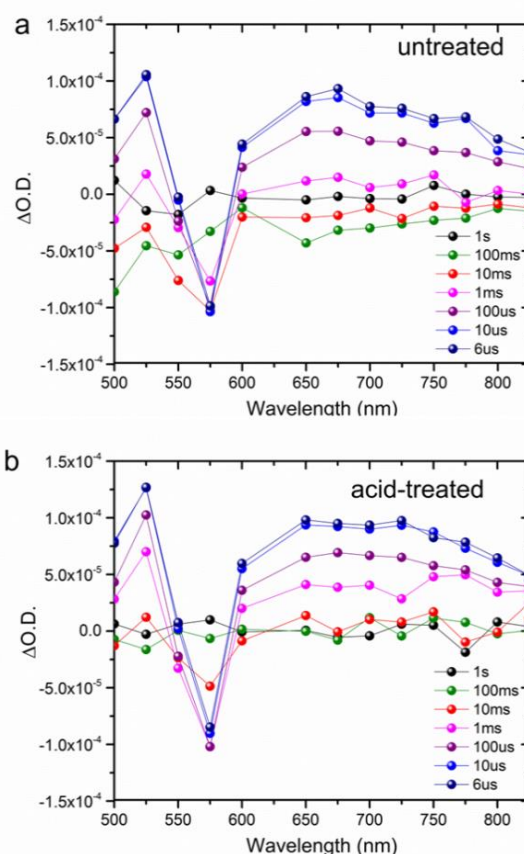

Fig 3. Full spectra TA under working photoelectrochemical conditions (355 nm excitation) at an applied voltage of 0.2 V vs. Ag/AgCl for a) untreated and b) acid treated hematite.

In summary, we have demonstrated that acid treatment can substantially increase the performance of hematite photoanodes for PEC water splitting. EIS studies have shown that enhanced photocurrent is partly due to improved efficiency of charge separation; and moreover, TA and TPC spectroscopic studies provide evidence that the improved efficiency can also be related to a minimization of surface electron-hole recombination brought about by an increased detrapping rate, in line with the improved conductivity and potential passivation of surface electron traps. We believe that present studies open up new opportunities for design and fabrication of high performance hematite electrodes for PEC reactions.
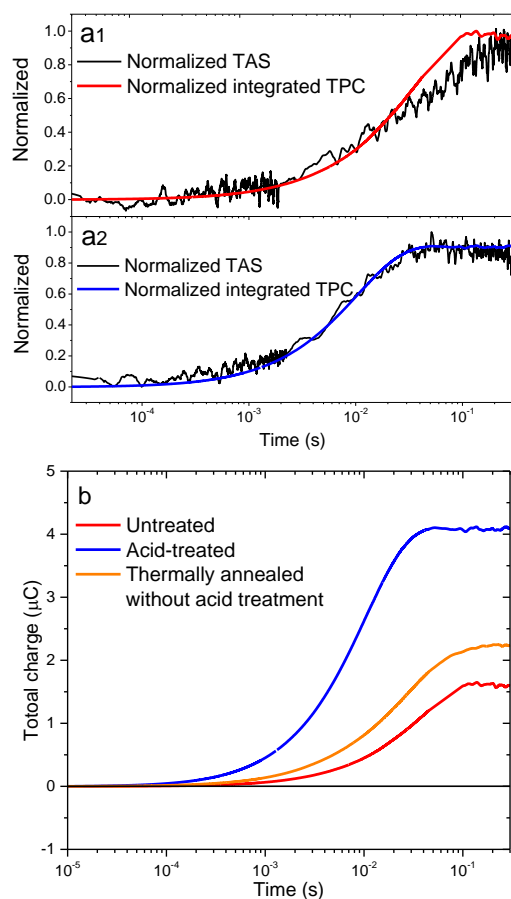
Fig 4. Overlay of 575 nm TA signal assigned to photoelectron trapping with the total charge passed derived from TPC folling 355 nm excitation of a1) untreated and a2) acid treated hematite at 0.2 V vs. Ag/AgCl. b) The charge extracted with time before normalization for the photoelectrodes studied.

Keywords: Hematite • acid treatment • metal oxides • photoelectrochemical water splitting • transient absorption spectroscopy

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COMMUNICATION

We report a new and simple acid treatment method to substantially increase photoelectrochemical activity of hematite photoanodes. We found that the enhanced photocurrent is due to improved efficiency of charge separation, as well as efficiently suppressed surface electron-hole recombination due to a greater yield of the trapped photoelectrons being extracted to the external circuit.
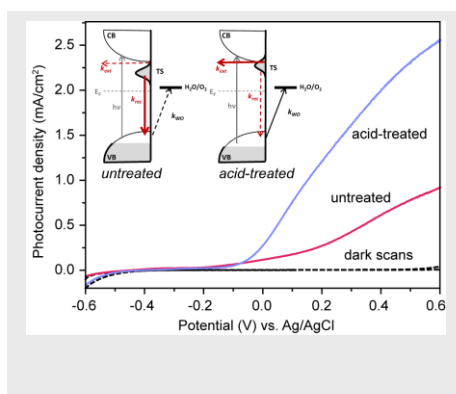
Yi Yang,[a] Mark Forster,[b] Yichuan Ling, [a] Gongming Wang, [a] Teng Zhai, [a],[c] Yexiang Tong,[c] Alexander J. Cowan*.[b] and Yat Li*.[a]

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