Reversible Charge Transfer and Adjustable Potential Window in Semiconductor/Faradaic Layer/Liquid Junctions

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HIGHLIGHTS
A new concept of a Faradaic junction is proposed
The photoelectrode performance is improved by eliminating short circuit contact
A characteristic of adjustable potential window in a Faradaic junction is reported

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Reversible Charge Transfer and Adjustable Potential Window in Semiconductor/Faradaic Layer/Liquid Junctions

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SUMMARY

Semiconductor/Faradaic layer/liquid junctions have been widely used in solar energy conversion and storage devices. However, the charge transfer mechanism of these junctions is still unclear, which leads to inconsistent results and low performance of these devices in previous studies. Herein, by using Fe2O3 and Ni(OH)2 as models, we precisely control the interface structure between the semiconductor and the Faradaic layer and investigate the charge transfer mechanism in the semiconductor/Faradaic layer/liquid junction. The results suggest that the short circuit severely restricts the performance of the junction for both solar water splitting cells and solar charging supercapacitors. More importantly, we also find that the charge-discharge potential window of a Faradaic material sensitively depends on the energy band positions of a semiconductor, which provides a new way to adjust the potential window of a Faradaic material. These new insights offer guidance to design high-performance devices for solar energy conversion and storage.

INTRODUCTION

Solar energy, as a green, renewable, and widely available energy source, plays an important role in achieving a sustainable society. In the past decades, various solar energy-harvesting technologies, such as solar cells, solar water-splitting cells, and solar charging supercapacitors, have attracted intensive attention (Yao et al., 2018; Jiang et al., 2017; Shi et al., 2016; Sun and Yan, 2017; Yi et al., 2018; Sun et al., 2018; Ma et al., 2019). Among them, semiconductor/liquid junctions are core structures in these devices. Electron-hole pairs are generated in semiconductors under irradiation, which are separated and transferred across the semiconductor/liquid interface. In these processes, the efficiencies of charge separation and transfer have critical effects on the performances of these devices. In previous studies, an intermediate layer, sandwiched between semiconductor and liquid, was widely used to improve the charge separation and transfer at the semiconductor/liquid interface. Usually, there are two kinds of intermediate layers, non-Faradaic and Faradaic (see Figure 1). A non-Faradaic intermediate layer, such as TiO2 and Al2O3, is inert, which is used to improve charge separation by built-in electric field (Lin et al., 2012; Boettcher et al., 2011; Luo et al., 2007) and surface passivation (Yu et al., 2017; Chen et al., 2011; Seger et al., 2013). In contrast, a Faradaic intermediate layer, such as Ni(OH)2, CoPi, and Fe3H4O8.3H2O, is electrochemically active, which captures/releases electrons from the semiconductor layer and at the same time reacts with the ions from the electrolyte to produce a new substance (Shao et al., 2018). It is worth of note that this Faradaic reaction is fast and reversible by controlling an applied potential, which leads to the intermediate layer regenerated. In previous studies, Faradaic intermediate layers were coated on the surfaces of semiconductor photoanodes as hole collectors (Liu et al., 2014; Li et al., 2018; Laskowski et al., 2019) and oxygen evolution catalysts (Kim and Choi, 2014; Lin and Boettcher, 2014; Zhong et al., 2011; Li et al., 2013; Wang et al., 2018), which enhanced both charge separation and transfer efficiency at the semiconductor/liquid interface. Therefore, Faradaic layers are more ideal than non-Faradaic layers for high-efficiency solar water-splitting cells. However, other reports suggested that the coating of Faradaic layers on semiconductor photoanodes decreased the performance of solar water splitting (Wang et al., 2013; Lim et al., 2017; Zhu et al., 2018). Since both the semiconductors and the Faradaic layers are the same (Liu et al., 2016; Young and Hamann, 2014; Steier et al., 2015), the inconsistent results in previous studies possibly originate from uncontrollable interface structures between semiconductors and Faradaic layers.

Moreover, some Faradaic layers, including Ni(OH)2 (Zhu et al., 2018; Xia et al., 2012; Wang et al., 2014) and PbO2 (Safshekan et al., 2017), have also been directly coated on the surface of semiconductors as photo charging supercapacitors for solar conversion and storage. In these devices, electron-hole pairs are...
generated in semiconductors under irradiation, which are injected into the Faradaic layers to be stored. When the light is off, the stored electrons or holes in the Faradaic layers are released as electricity. The photo charge and dark discharge are also reversible owing to the Faradaic reaction. In conventional supercapacitors, Faradaic layers on conductive substrates can be charged completely in dark. However, in solar charging supercapacitors, only a little part of Faradaic layers are photo-charged on semiconductors, which leads to much lower specific capacitances in solar charging supercapacitors than conventional supercapacitors (Zhu et al., 2018; Xia et al., 2012; Sekhar et al., 2017; Chang et al., 2014). It is not clear whether the charging processes on semiconductors are different from those on conductive substrates or not. Although semiconductor/Faradaic layer/liquid junctions (denoted as Faradaic junctions) have been used in solar water splitting cells and solar charging supercapacitors, the charge transfer mechanism is still unclear because the charge carriers in a Faradaic material are coupled electrons and ions, which are essentially different from electrons or ions in other conventional semiconductor junctions, such as p-n junctions, Schottky or Schottky-like junctions, and Ohmic contacts (see Figure S1). Therefore, it is desirable to understand the charge transfer mechanism in a Faradaic junction, not only to improve the performances of both solar water-splitting cells and solar charging supercapacitors, but also to provide possibilities to construct some new devices.

Herein, we report on a charge transfer mechanism in Faradaic junctions by controlling the Faradaic layers shorted or isolated with conductive substrates. Fe$_2$O$_3$ semiconductors and Ni(OH)$_2$ Faradaic layers were used as model materials. Ni(OH)$_2$ was selectively deposited on different positions of Fe$_2$O$_3$ nanorods by chemical bath deposition (CBD) and photoelectrodeposition (PED), and the fabricated samples are labeled as C-Fe$_2$O$_3$/Ni(OH)$_2$ and P-Fe$_2$O$_3$/Ni(OH)$_2$, respectively. We found that water oxidation reaction was completely restrained in C-Fe$_2$O$_3$/Ni(OH)$_2$ under illumination, whereas it was accelerated in P-Fe$_2$O$_3$/Ni(OH)$_2$. Moreover, only a small part of the Ni(OH)$_2$ in C-Fe$_2$O$_3$/Ni(OH)$_2$ was photoelectrochemically oxidized into NiOOH, but the Ni(OH)$_2$ in P-Fe$_2$O$_3$/Ni(OH)$_2$ was mostly oxidized into NiOOH under illumination. Further analysis suggested that the short circuit contact between the Faradaic layer and the conductive substrate was the reason for inconsistent results in solar water splitting and much lower specific capacitance in solar charging supercapacitors. By eliminating the short circuit contact, the performances of both solar water splitting cells and solar charging supercapacitors were improved remarkably. Moreover, we also found that the potential barrier heights between Faradaic materials and conductive substrates were negligible, whereas high-potential barriers formed between Faradaic materials and semiconductors, which led to the shift of a charge-discharge potential window of a Faradaic material. The potential window of a Faradaic material is a significant parameter in the construction of a supercapacitor full device (Shao et al., 2018). The barrier heights can be controlled by the band position of semiconductors, which suggests a new way to adjust the potential window of a Faradaic material by introducing a semiconductor layer.

RESULTS AND DISCUSSION

Fe$_2$O$_3$ nanorod arrays were hydrothermally grown on fluorine-doped tin oxide (FTO) substrates following previous studies (Liao et al., 2018). Ni(OH)$_2$ was coated on Fe$_2$O$_3$ nanorods by CBD and PED methods (see
Supplemental Information for details). The XRD pattern of Fe₂O₃/Ni(OH)₂ is shown in Figure S2. Only peaks of α-Fe₂O₃ and FTO substrates are observed. Figures 2A–2C and S3A–S3C indicate the cross-section and top-view SEM images of bare Fe₂O₃, C-Fe₂O₃/Ni(OH)₂, and P-Fe₂O₃/Ni(OH)₂, respectively. Some cavities are observed between the nanorods in bare Fe₂O₃ (see Figures 2A and S3A). After coating of Ni(OH)₂ on Fe₂O₃ by CBD, the whole Fe₂O₃ nanorods are covered completely by Ni(OH)₂, including the cavities between the nanorods, and part of the Ni(OH)₂ layer contacts directly with FTO substrates (see Figures 2B and S3B). In contrast, the PED process creates Ni(OH)₂ nanoflakes exclusively on the top of Fe₂O₃ nanorods and no Ni(OH)₂ contacts with FTO substrate directly (see Figures 2C and S3C). The dyeing details of the cross-section SEM image P-Fe₂O₃/Ni(OH)₂ are shown in Figure S4. The different deposition behaviors of Ni(OH)₂ in C-Fe₂O₃/Ni(OH)₂ and P-Fe₂O₃/Ni(OH)₂ samples are explained in the Supplemental Information. Moreover, TEM was also used to characterize the morphologies of these two Fe₂O₃/Ni(OH)₂ samples by CBD and PED, and the results are shown in Figures 2D and 2E, respectively. The C-Fe₂O₃/Ni(OH)₂ sample has a core-shell structure with the Ni(OH)₂ shell thickness of 6 nm. The surface of the P-Fe₂O₃/Ni(OH)₂ is covered by Ni(OH)₂ nanoflakes, which is in agreement with the SEM results. To further reveal the Ni(OH)₂ distributions, the XPS depth profile was used to analyze the samples by Ar⁺ etching and the results are indicated in Figures 2F–2H. The binding energy at 856.3 eV with a satellite peak at 862.1 eV on the surfaces of the two samples by CBD and PED is assigned to Ni 2p (Ji et al., 2013; Zhu et al., 2017a, 2017b). A new peak at 853.1 eV appears at different depths of the two samples owing to the reduction of Ni²⁺ into metallic Ni by Ar⁺ etching (Kim and Winograd, 1974). The intensities of XPS peaks of Ni 2p at different depths in C-Fe₂O₃/Ni(OH)₂ are similar, whereas the intensities in P-Fe₂O₃/Ni(OH)₂ become lower with the etching depths increasing until the peaks disappear. Figure 2H indicates the ratios of Ni/Fe at different depths of C-Fe₂O₃/Ni(OH)₂ and P-Fe₂O₃/Ni(OH)₂.
depths of C-Fe$_2$O$_3$/Ni(OH)$_2$ and P-Fe$_2$O$_3$/Ni(OH)$_2$. In C-Fe$_2$O$_3$/Ni(OH)$_2$, the ratios of Ni/Fe are almost the same at different depths except for a little higher value on the surface, which suggests that Ni$^{2+}$ uniformly distributes in the whole Fe$_2$O$_3$ film and some Ni(OH)$_2$ contacts with FTO substrate directly. However, the ratios of Ni/Fe decrease gradually to a negligible level at the depth of 300 nm in P-Fe$_2$O$_3$/Ni(OH)$_2$, which suggests that Ni(OH)$_2$ distributes only on the top of the Fe$_2$O$_3$ film and no Ni(OH)$_2$ contacts with the FTO substrate directly.

To reveal the charge transfer mechanism in the Faradaic junction, the electrochemical and photoelectrochemical properties of C-Fe$_2$O$_3$/Ni(OH)$_2$ and P-Fe$_2$O$_3$/Ni(OH)$_2$ were measured in 1 M KOH aqueous solution. If not specifically mentioned, light is illuminated from the Fe$_2$O$_3$/Ni(OH)$_2$/electrolyte interface. As a reference sample, Ni(OH)$_2$ was first directly deposited on an FTO substrate by CBD method. In the dark, the colorless Ni(OH)$_2$ on FTO substrate becomes black after being oxidized into NiOOH at the potential of 1.46 V versus reversible hydrogen electrode (RHE) (see Figure 3A) (Zhu et al., 2017a, 2017b). The C-Fe$_2$O$_3$/Ni(OH)$_2$ becomes dark red from red at the same potential in the dark (see Figure 3B). Since the color of a bare Fe$_2$O$_3$ does not change in the dark at the same potential (see Figure S5A), the changed color comes from oxidation of Ni(OH)$_2$ in C-Fe$_2$O$_3$/Ni(OH)$_2$ by transferring electrons to FTO directly. In contrast, neither redox peak nor color change is observed on P-Fe$_2$O$_3$/Ni(OH)$_2$ at the whole potential range of 0.3 V–1.7 V versus RHE in dark (see Figure 3B), suggesting the highly chemical resistance to oxidation of Ni(OH)$_2$ in this case. Figure 3C shows the cyclic voltammetry curves of C-Fe$_2$O$_3$/Ni(OH)$_2$ with different scan rates under illumination. The C-Fe$_2$O$_3$/Ni(OH)$_2$ shows two pairs of redox peaks. When the scan rate is 10 mV/s, an oxidation peak at 0.93 V versus RHE is observed and no photocurrent is observed at the potential range of 1.1–1.3 V versus RHE. The peak intensity and width increase with increase in the scan rate, which suggests the photocurrent comes from holes-induced capacitive current (Tian et al., 2013). The color of C-Fe$_2$O$_3$/Ni(OH)$_2$ changes from red to dark red after the first oxidation peak. The color of a bare Fe$_2$O$_3$ does not change under illumination at the same potential (see Figure S5B), indicating Ni(OH)$_2$ is oxidized into NiOOH. Moreover, C-Fe$_2$O$_3$/Ni(OH)$_2$ does not change color in the dark in this range (see Figure 3B) and the photocurrent of the first peak comes from the oxidation of Ni(OH)$_2$ by photo-generated holes in Fe$_2$O$_3$. In order to further confirm that the photocurrent of the first peak does not come from water oxidation, I-t curves of C-Fe$_2$O$_3$/Ni(OH)$_2$ were also measured under illumination (see Figure 3E). The photocurrent decays quickly and negligible steady photocurrent is obtained at all selected potentials. According to previous studies (Wang et al., 2013; Zhu et al., 2018), the transient photocurrent comes from Ni(OH)$_2$ oxidation and the photocurrent will disappear once all of Ni(OH)$_2$ is oxidized into NiOOH. The steady photocurrent comes from water oxidation. When water is oxidized into O$_2$, some other water molecules in the electrolyte will diffuse to the electrode surface to maintain the water concentrations. Therefore, the photocurrent is stable. The present results suggest that water oxidation reaction is completely suppressed in C-Fe$_2$O$_3$/Ni(OH)$_2$. After C-Fe$_2$O$_3$/Ni(OH)$_2$ is scanned at the second peak (1.5 V versus RHE), the color of the sample becomes deeper and more Ni(OH)$_2$ is oxidized at this potential. Similar oxidation current is also observed at the same potential in FTO/Ni(OH)$_2$ in the dark (see Figure 3A). Therefore, the oxidation current of C-Fe$_2$O$_3$/Ni(OH)$_2$ at the second peak comes from electrochemical oxidation of Ni(OH)$_2$. After Ni(OH)$_2$ is mostly oxidized into NiOOH, water oxidation starts (Cibrev et al., 2013). When the light is off, two reduction peaks at 1.29 and 0.7 V versus RHE are observed in C-Fe$_2$O$_3$/Ni(OH)$_2$ (see Figure 3C). The color of C-Fe$_2$O$_3$/Ni(OH)$_2$ becomes lighter after the second reduction peak (1.29 V versus RHE). This reduction peak is very close to that of Ni(OH)$_2$ on FTO substrates (see Figure 3A), which suggests it comes from the reduction of NiOOH by electrons from the FTO substrate. However, the color of the film does not completely recover after the second reduction peak (1.29 V versus RHE), indicating some NiOOH cannot be reduced by electrons from the FTO substrate, possibly blocked by Fe$_2$O$_3$. After the first reduction peak (0.7 V versus RHE), the color of C-Fe$_2$O$_3$/Ni(OH)$_2$ completely recovers into red. The results suggest that the remaining NiOOH is reduced by electrons from Fe$_2$O$_3$.

In P-Fe$_2$O$_3$/Ni(OH)$_2$, two obvious oxidation peaks are observed when the scan rate is 10 mV/s under illumination. The first oxidation peak is at 0.8 V versus RHE. The peak intensity and width increase with increase in scan rate, which suggests that the photocurrent comes from holes-induced capacitive current (Tian et al., 2013). When the scan rates are higher (30 and 50 mV/s), the intensity of the first peak increases and the peak position shifts positively, which leads to an overlap between the first and the second peaks. The color of P-Fe$_2$O$_3$/Ni(OH)$_2$ changes from red to dark red after the first peak, indicating Ni(OH)$_2$ is oxidized into NiOOH. The second oxidation peak is very wide, and its intensity and width are independent on the scan rates. In order to further confirm the origin of the photocurrent, I-t curves of P-Fe$_2$O$_3$/Ni(OH)$_2$ were also measured at
different potentials under illumination (see Figure 3F). I-t curve at 0.8 V versus RHE decays to zero after about 70 s. As mentioned above, the transient photocurrent and the steady photocurrent come from Ni(OH)$_2$ oxidation and water oxidation, respectively. This result suggests that no water oxidation happens at 0.8 V versus RHE and all the photocurrent at this potential comes from Ni$^{2+}$ oxidation. When the potential is higher than 0.9 V versus RHE, the photocurrent of P-Fe$_2$O$_3$/Ni(OH)$_2$ initially decays and then keeps constant. After Ni(OH)$_2$ is mostly oxidized into NiOOH, the photocurrent becomes stable for water oxidation. Therefore, the second peak comes from water oxidation. After the reduction peak, P-Fe$_2$O$_3$/Ni(OH)$_2$ becomes red (see Figure 3D), which suggests that NiOOH is reduced by electrons from Fe$_2$O$_3$ since no Ni(OH)$_2$ contacts with FTO directly in the sample.

Moreover, the water oxidation photocurrent of Fe$_2$O$_3$ at 1.0 V versus RHE is enhanced and its onset potential is also negatively shifted after coating Ni(OH)$_2$ (see Figures 3G and S6A). I-t curve of P-Fe$_2$O$_3$/Ni(OH)$_2$ at 1.0 V versus RHE is also measured for 3.5 h. After 0.8 h, the photocurrent gradually decays to about 80% of the initial photocurrent and then keeps stable (see Figure S6B). Cyclic voltammetry (CV) and i-t curves of AB

Figure 3. (Photo)electrochemical Properties of Ni(OH)$_2$, Fe$_2$O$_3$, and Fe$_2$O$_3$/Ni(OH)$_2$ Electrodes

Cyclic voltammetry (CV) curves of FTO/Ni(OH)$_2$ (A), C-Fe$_2$O$_3$/Ni(OH)$_2$, and P-Fe$_2$O$_3$/Ni(OH)$_2$ (B) in the dark; CV curves of C-Fe$_2$O$_3$/Ni(OH)$_2$ (C) and P-Fe$_2$O$_3$/Ni(OH)$_2$ (D) with different scan rates under illumination; i-t curves of C-Fe$_2$O$_3$/Ni(OH)$_2$ (E) and P-Fe$_2$O$_3$/Ni(OH)$_2$ (F) at different potentials under illumination. I-t curves of C-Fe$_2$O$_3$/Ni(OH)$_2$, P-Fe$_2$O$_3$/Ni(OH)$_2$, and bare Fe$_2$O$_3$ at 1.0 V versus RHE under illumination (G). Insets in (A–D) are the photos of FTO/Ni(OH)$_2$ or Fe$_2$O$_3$/Ni(OH)$_2$ samples at different potentials. Scan rate: 30 mV/s (if not specifically mentioned), light source: AM 1.5 G sunlight simulator, electrolyte: 1 M KOH aqueous solution. See also Figures S5–S8 and Table S1.
bared Fe$_2$O$_3$ and P-Fe$_2$O$_3$/Ni(OH)$_2$ were measured from front and back illumination and the results are shown in Figures S7A and S7B. Higher performance is obtained from front illumination than from back illumination, because most of Ni(OH)$_2$ distributes at the front side of Fe$_2$O$_3$ (the interface between the Fe$_2$O$_3$ and electrolyte) in P-Fe$_2$O$_3$/Ni(OH)$_2$. These results suggest that NiOOH serves as a Faradaic electrocatalyst for water oxidation, leading to a faster charge separation rate at the surface of Fe$_2$O$_3$. Water oxidation is enhanced in P-Fe$_2$O$_3$/Ni(OH)$_2$. However, it is completely suppressed in C-Fe$_2$O$_3$/Ni(OH)$_2$. In previous studies, some inconsistent results (improved or decreased water oxidation photocurrent) have been reported on Ni(OH)$_2$-coated Fe$_2$O$_3$ photoanodes (Wang et al., 2013; Lim et al., 2017; Zhu et al., 2018; Liu et al., 2016; Young and Hamann, 2014; Steier et al., 2015). According to the above analysis, it is proposed that the reasons are the different distributions of Ni(OH)$_2$ on Fe$_2$O$_3$ nanorods. If Ni(OH)$_2$ contacts with an FTO conductive substrate, the water oxidation performance of an Fe$_2$O$_3$ photoanode will be decreased. In contrast, if Ni(OH)$_2$ does not contact with an FTO conductive substrate, the water oxidation performance will be improved.

The specific capacitances of C-Fe$_2$O$_3$/Ni(OH)$_2$ and P-Fe$_2$O$_3$/Ni(OH)$_2$ as solar charging supercapacitors were measured, and the results are shown in Table S1. The experimental capacitance of Ni(OH)$_2$ in C-Fe$_2$O$_3$/Ni(OH)$_2$ is 350 C/g, only 33.7% of the theoretical value. In contrast, the experimental capacitance of Ni(OH)$_2$ in P-Fe$_2$O$_3$/Ni(OH)$_2$ is 804.6 C/g (77.4% of the theoretical value), much higher than the value in C-Fe$_2$O$_3$/Ni(OH)$_2$. The value is close to that of a conventional supercapacitor (790.3 C/g) (Shao et al., 2018). In a conventional supercapacitor, the capacitance is obtained by electrochemical charging. However, in this study, the high-capacitance supercapacitor is obtained by light charging, which can be used to store solar energy directly. Therefore, by eliminating the short circuit, the performance of a P-Fe$_2$O$_3$/Ni(OH)$_2$ electrode is significantly increased both in a solar water-splitting cell and in a solar charging supercapacitor.

An equilibrium potential is used to further understand the reversible redox process of Ni(OH)$_2$ on the two Fe$_2$O$_3$ samples by CBD and PED. At an equilibrium potential, oxidation and reduction rates of Ni(OH)$_2$ ↔ NiOOH are the same. The equilibrium potential of Ni(OH)$_2$ ↔ NiOOH is about 1.38 V versus RHE on FTO (See Figure S8A). If an applied potential is more positive than the equilibrium potential, the amount of NiOOH is higher than Ni(OH)$_2$ on the FTO substrate. In contrast, if an applied potential is more negative than the equilibrium potential, the amount of NiOOH is lower than Ni(OH)$_2$ on an FTO substrate. Notwithstanding the negative shift of Ni(OH)$_2$ ↔ NiOOH equilibrium potential from 1.38 V versus RHE to 0.74 V versus RHE on Fe$_2$O$_3$, the total equilibrium potential of Ni(OH)$_2$ ↔ NiOOH on C-Fe$_2$O$_3$/Ni(OH)$_2$ is still 1.38 V versus RHE owing to the direct contact of Ni(OH)$_2$ with an FTO substrate (see Figure S3C). However, the onset potential of dark charge is 1.37 V versus RHE (see Figure S8A), slightly lower than the total equilibrium potential of 1.38 V versus RHE. If the potential is higher than the onset potential of dark charge, the photo current charge is negligible. Therefore, only part of Ni(OH)$_2$ can be oxidized in C-Fe$_2$O$_3$/Ni(OH)$_2$ at potentials of 0.72 V–1.37 V versus RHE even under illumination. By contrast, the total equilibrium potential of Ni(OH)$_2$ ↔ NiOOH on P-Fe$_2$O$_3$/Ni(OH)$_2$ is 0.74 V versus RHE (see Figure S8B) since Ni(OH)$_2$ does not contact with an FTO conductive substrate directly. Therefore Ni(OH)$_2$ is mostly oxidized into NiOOH on P-Fe$_2$O$_3$/Ni(OH)$_2$ under illumination and then acts as Faradaic electrocatalyst for water oxidation.

Based on the above results, a general charge transfer mechanism in a Faradaic junction is proposed as follows. Figures 4A–4C show charge transfer in Fe$_2$O$_3$/Ni(OH)$_2$. Faradaic junctions during dark charge, photo charge, and dark discharge, respectively. For C-Fe$_2$O$_3$/Ni(OH)$_2$ sample during dark charge, Ni(OH)$_2$ contacts with FTO and can then be oxidized by transferring electrons to FTO (see Figure 4A). Meanwhile, Ni(OH)$_2$ releases H$^+$ ions into electrolyte to maintain electric neutrality. However, Ni(OH)$_2$ cannot be oxidized even at a very positive potential in P-Fe$_2$O$_3$/Ni(OH)$_2$ sample as it does not contact with FTO. There is no electron and ion transfer in P-Fe$_2$O$_3$/Ni(OH)$_2$ because there are no holes in Fe$_2$O$_3$ in the dark. When C-Fe$_2$O$_3$/Ni(OH)$_2$ is illuminated, Ni(OH)$_2$ can be photo-oxidized into NiOOH by donating electrons to Fe$_2$O$_3$, which then transfer to the FTO substrate (see Figure 4B). Noticeably, the oxidation product (NiOOH) has much lower resistance than Fe$_2$O$_3$ (see Table S2) and thereby leads to short circuit. In this condition, electrons prefer to back-transfer from FTO to NiOOH, and then reduce NiOOH to Ni(OH)$_2$ on which water oxidation reaction cannot occur, whereas for P-Fe$_2$O$_3$/Ni(OH)$_2$, in which Ni(OH)$_2$ does not contact with FTO and thus has no short circuit, electrons can only transfer from Ni(OH)$_2$ to Fe$_2$O$_3$ under illumination until Ni(OH)$_2$ is mostly photo-oxidized into NiOOH (see Figure 4B). And then NiOOH serves as Faradaic electrocatalyst for water oxidation and improves the performance of solar water splitting. The short circuit results in the poor performance in a Faradaic layer-coated photoelectrode for solar water splitting. If the short circuit exists, water oxidation reaction will be suppressed. If not, water oxidation
will be accelerated. This is the main reason for inconsistent results on a Faradaic layer-coated semiconductor photoelectrode for solar water splitting in previous studies (Wang et al., 2013; Lim et al., 2017; Zhu et al., 2018; Liu et al., 2016; Young and Hamann, 2014; Steier et al., 2015). Moreover, the short circuit also leads to partial oxidization of Faradaic layer in a photo-supercapacitor, which intrinsically decreases the specific capacitance.

During dark discharge, there are two electron transfer paths, from Fe₂O₃ or FTO to NiOOH, in C-Fe₂O₃/Ni(OH)₂ (Figure 4C), which lead to two reduction peaks in CV curves (see Figure 3C), whereas in P-Fe₂O₃/Ni(OH)₂, electrons can only transfer from Fe₂O₃ to NiOOH and only one reduction peak is observed in CV curves (see Figure 3D).

In order to understand different charge transfer behaviors of a Faradaic layer on a conductive substrate and on a semiconductor, we also investigated the potential windows of a Faradaic layer on different conductive substrates and semiconductors. Ni(OH)₂ was coated on FTO, carbon paper, and Pt foil by electrodeposition (see Supplemental Information). Figure 5A shows the CV curves of FTO/Ni(OH)₂, C/Ni(OH)₂, and Pt/ Ni(OH)₂ in the dark, respectively. Although the Fermi levels of the three conductive substrates are quite different (Andersson et al., 1998; Shin et al., 2008; Axnanda et al., 2013), the equilibrium potentials of the redox reaction (Ni(OH)₂ ↔ NiOOH) are still the same (1.36 V versus RHE). The galvanostatic charge-discharge (GCD) curves (see Figure 5B) also further confirm that the conductive substrates cannot change the charge-discharge potential windows of the Faradaic material by adjusting the Fermi levels of conductive substrates. Obviously different phenomena are observed on semiconductors. Ni(OH)₂ was coated on the top of Fe₂O₃ (P-Fe₂O₃/Ni(OH)₂) and TiO₂ nanorods (P-TiO₂/Ni(OH)₂) by the PED method, respectively. The CV curves of P-TiO₂/Ni(OH)₂ with sample photos at different potentials are shown in Figure S9B. Similar to P-Fe₂O₃/Ni(OH)₂, I-t curves of P-TiO₂/Ni(OH)₂ indicate transient photocurrent and steady photocurrent, which come from Ni(OH)₂ oxidation and water oxidation, respectively (see Figure S10). In contrast, the equilibrium potential of Ni(OH)₂ ↔ NiOOH (photo oxidation and dark reduction) shifts to 0.74 V versus RHE and 0.19 V versus RHE on Fe₂O₃ and TiO₂ (Figure 5C), respectively, much negative than the equilibrium potential (1.36 V versus RHE) on FTO conductive substrate. The photo oxidation peak and the dark reduction peak on P-Fe₂O₃/Ni(OH)₂ and P-TiO₂/Ni(OH)₂ are asymmetrical because part of photocurrent comes from water oxidation. Similarly, the photo charge-dark discharge potential windows of Ni(OH)₂ ↔ NiOOH also shift negatively on Fe₂O₃ and TiO₂ in GCD curves (Figure 5D). The potential window of a Faradaic material is the same on different conductive substrates, but it shifts remarkably on different semiconductors. This phenomenon can be explained as follows. The band positions of Fe₂O₃ and TiO₂ are obtained from the literature (Kment et al., 2017). When a Faradaic material contacts with a conductive substrate, the Fermi level of a conductive substrate is shifted to the redox potential (Ni(OH)₂ ↔ NiOOH) and the potential barrier height is negligible (see Figure 5E). However, on a semiconductor, a potential barrier forms and the Faradaic layer (Ni(OH)₂ ↔ NiOOH) is blocked from the FTO substrate by a semiconductor (Fe₂O₃ or

**Figure 4. A Proposed Charge Transfer Mechanism in Faradaic Junctions**

A proposed charge transfer mechanism in C-Fe₂O₃/Ni(OH)₂ and P-Fe₂O₃/Ni(OH)₂ during dark charge (A), photo charge (B), and dark discharge (C). See also Table S2.
The potential barrier height ($\Delta$V) is the difference between the conduction band position of an n-type semiconductor and the redox potential of Ni(OH)$_2$ or NiOOH. Therefore, the redox reaction of Ni(OH)$_2$ or NiOOH will happen only when the conduction band position of the semiconductor shifts to the flat band position under a given negative potential (see Figure 5F). Therefore, the photocharge-dark discharge potential windows of Ni(OH)$_2$ or NiOOH are adjusted by the conduction band positions of Fe$_2$O$_3$ or TiO$_2$. This is the first case to report on the dependence of a potential window of a Faradaic material on the energy band positions of a semiconductor, which provides guidance for designing solar charging supercapacitors. The potential windows of a positive electrode and a negative electrode are both significant for the performance of a supercapacitor full device. For a Faradaic material in a conventional supercapacitor, its electrochemical potential window is fixed. This study also suggests a new way to adjust the potential window of a Faradaic material by introducing a semiconductor layer, which provides possibilities to construct new devices.

Conclusion
A general charge transfer mechanism in a semiconductor/Faradaic layer/liquid junction was elucidated by using Fe$_2$O$_3$ and Ni(OH)$_2$ as model materials. A Faradaic layer of Ni(OH)$_2$ directly contacted with

Figure 5. Different Charge Transfer Behaviors of a Faradaic Layer on a Conductive Substrate and on a Semiconductor
Cyclic voltammetry (CV) (A) and galvanostatic charge-discharge (GCD) (B) curves of Ni(OH)$_2$ on FTO, C and Pt conductive substrates with different Fermi levels in the dark; cyclic voltammetry (CV) (C) and galvanostatic charge-discharge (GCD) (D) curves of FTO/Ni(OH)$_2$, P-Fe$_2$O$_3$/Ni(OH)$_2$, and P-TiO$_2$/Ni(OH)$_2$ under illumination and in the dark; band diagrams of the interfaces between FTO/Ni(OH)$_2$, C/Ni(OH)$_2$, and Pt/Ni(OH)$_2$ (E) and band diagrams of the interfaces between FTO/Ni(OH)$_2$, FTO/Fe$_2$O$_3$/Ni(OH)$_2$, and FTO/TiO$_2$/Ni(OH)$_2$ under an applied potential (F), $\Delta$V is the barrier height. Scan rate: 30 mV/s; light source: AM 1.5 G sunlight simulator; electrolyte: 1 M KOH aqueous solution. See also Figures S9–S11.
both the semiconductor and the conductive substrate in the sample led to two kinds of electron transfer paths, one was from the semiconductor to the Faradaic layer and the other was short circuit from the conductive substrate to the Faradaic layer. The short circuit contact led to a serious decrease of the performances of both solar water-splitting cells and solar charging supercapacitors. By eliminating the short circuit contact, the performances of the devices were improved remarkably. A blocking layer can be introduced between a semiconductor and a conductive substrate to further eliminate short circuit contact and improve the performances of devices. Moreover, the potential barrier heights between Faradaic materials and conductive substrates with different Fermi levels were negligible, whereas obvious potential barrier formed between the Faradaic materials and semiconductors, which led to the shift of a potential window of a Faradaic material. The charge-discharge potential window of a Faradaic material is very important in the supercapacitor full device construction. This finding provides a new way to adjust the potential window of a Faradaic material by introducing a semiconductor layer. The Faradaic layer plays a key role in a semiconductor/Faradaic layer/liquid junction, which is a bridge between the semiconductor and the liquid to exchange charges. This work provides insight and opens up new opportunities in the rational design and development of high-performance semiconductor/Faradaic layer/liquid junctions for solar energy conversion and storage.

Limitations of the Study
In this study, by eliminating short circuit contact in a Faradaic junction photoelectrode, its performance in both solar water splitting and solar charging supercapacitors has been improved. However, the preparation method of the Faradaic layer needs to be further explored to obtain a higher mass loading. Besides, the photoelectrode as a solar charging supercapacitor was only measured in a three-electrode cell. A full device needs to be constructed in future.

METHODS
All methods can be found in the accompanying Transparent Methods supplemental file.

SUPPLEMENTAL INFORMATION
Supplemental Information can be found online at https://doi.org/10.1016/j.isci.2020.100949.

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AUTHOR CONTRIBUTIONS
W.L. and Z.Z. proposed the project. W.L. conceived the concept and designed the experiments. X.C. prepared the samples, characterized the samples, and carried out electrochemistry measurement; W.L. and X.C. analyzed the data and wrote the paper. All authors discussed the results and gave comments on the manuscript.

DECLARATION OF INTERESTS
The authors declare no competing interests.

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Supplemental Information

Reversible Charge Transfer
and Adjustable Potential Window
in Semiconductor/Faradaic Layer/Liquid Junctions

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Figure S1. Different kinds of semiconductor junctions. The charge carriers in different materials are also listed below. Related to Figure 1.

| Materials    | Charge carrier         |
|--------------|------------------------|
| Conductor    | electron               |
| Semiconductor| electron or hole        |
| Electrolyte  | ion                    |
| Farador      | coupled electron and ion|

Figure S2. XRD patterns of C-Fe$_2$O$_3$/Ni(OH)$_2$. Related to Figure 2.

Figure S3. Top-view SEM images of bare Fe$_2$O$_3$ (a), C-Fe$_2$O$_3$/Ni(OH)$_2$ (b) and P-Fe$_2$O$_3$/Ni(OH)$_2$ (c). Related to Figure 2.
Figure S4. Dyeing details of a cross-section SEM image of P-Fe₂O₃/Ni(OH)₂ (red: Fe₂O₃, purple: Ni(OH)₂, green: FTO). Related to Figure 2.

Figure S5. CV curves of bare Fe₂O₃ in dark (a) and under illumination (b). Insets are the photos of the samples at different potentials. Scan rate: 30 mV/s, Light source: AM 1.5 G sunlight simulator, electrolyte: 1 M KOH aqueous solution. Related to Figure 3.
**Figure S6.** CV curves of P-Fe$_2$O$_3$/Ni(OH)$_2$ and bare Fe$_2$O$_3$ under illumination (a) and long-term i-t curve of P-Fe$_2$O$_3$/Ni(OH)$_2$ at 1.0 V vs. RHE (b). Scan rate: 30 mV/s, light source: AM 1.5 G sunlight simulator, electrolyte: 1 M KOH aqueous solution. Related to Figure 3.

**Figure S7.** CV curves (a) and i-t curves at 0.9 V vs. RHE (b) of bare Fe$_2$O$_3$ and P-Fe$_2$O$_3$/Ni(OH)$_2$ under front illumination and back illumination. Light is illuminated from the Fe$_2$O$_3$/Ni(OH)$_2$/electrolyte interface under front illumination, and illuminated from the Fe$_2$O$_3$/substrate interface under back illumination.

The bare Fe$_2$O$_3$ indicates similar photocurrent-potential curves from front illumination and back illumination. However, the P-Fe$_2$O$_3$/Ni(OH)$_2$ indicates a more negative onset potential under front illumination than that under back illumination (see Figure S7a), which suggests that higher performance is obtained from front illumination than that from back illumination. The i-t curves at 0.9 V vs. RHE further confirm the sample indicates higher photocurrent from front illumination than that from back illumination (see Figure S7b). This result can be explained as follows. When illuminated from the front side, most of carriers are photo-generated at the interface between Fe$_2$O$_3$ and Ni(OH)$_2$. When illuminated from back side, most of carriers are photo-generated at the interface between Fe$_2$O$_3$ and FTO substrates, where there is less Ni(OH)$_2$. Ni(OH)$_2$ is oxidized into NiOOH and serves as electrocatalyst, which leads to higher performance. Therefore, Ni(OH)$_2$ can improve charge separation at the interface.

However, the photocurrent at high potential (1.4 V~1.6 V vs. RHE) from front illumination is lower than that of from back illumination. It is because when Ni(OH)$_2$ is mostly oxidized into NiOOH, the sample becomes black, which blocks incident light and leads to lower performance. Therefore, the Ni(OH)$_2$ layer decreases charge generation in a photoelectrode. Related to Figure 3.
Figure S8. Schematic diagrams to estimate an equilibrium potential and an onset potential from CV curves of FTO/Ni(OH)$_2$ (a) and P-Fe$_2$O$_3$/Ni(OH)$_2$ (b). Equilibrium potentials in this article are all obtained by selecting a potential at which the oxidation current equals to the reduction current of Ni(OH)$_2$ ↔ NiOOH. An onset oxidation potential is estimated from the intercept by extrapolating the linear region of the oxidation peak to zero current density. Related to Figure 3.

Table S1. The loading masses of Ni(OH)$_2$, experimental and theoretical specific capacitance of Ni(OH)$_2$ in C-Fe$_2$O$_3$/Ni(OH)$_2$ and P-Fe$_2$O$_3$/Ni(OH)$_2$. Related to Figure 3.

| Samples | The loading mass of Ni(OH)$_2$ | Experimental specific capacitance (C$_E$) | Theoretical specific capacitance (C$_T$) | C$_E$/C$_T$ |
|---------|-------------------------------|------------------------------------------|------------------------------------------|------------|
| CBD     | 30 µg/cm$^2$                  | 350 C/g                                  | 1039.2 C/g                               | 33.7%      |
| PED     | 8.7 µg/cm$^2$                 | 804.6 C/g                                | 1039.2 C/g                               | 77.4%      |
Table S2. The electronic conductivities of FTO, α-Fe₂O₃, TiO₂, Ni(OH)₂ and NiOOH from literatures. Related to Figure 4.

| Materials    | Electronic conductivity | References          |
|--------------|-------------------------|---------------------|
| FTO          | $1 \times 10^{-3}$ Ω⁻¹cm⁻¹ | Benhaoua et al., 2014 |
| α-Fe₂O₃      | $10^{-14}$ Ω⁻¹cm⁻¹      | Lee et al., 2012    |
| TiO₂         | $10^{-6}$ Ω⁻¹cm⁻¹       | Dy et al., 2010     |
| Ni(OH)₂      | $10^{-13}$ Ω⁻¹cm⁻¹      | Deabate et al., 2003 |
| NiOOH        | $1$ Ω⁻¹cm⁻¹             | Tuomi et al., 1965  |

Figure S9. CV curves of C-TiO₂/Ni(OH)₂ (a) and P-TiO₂/Ni(OH)₂ (b) under illumination. Insets are the photos of the samples at different potentials. Scan rate: 30 mV/s, light source: AM 1.5 G sunlight simulator, electrolyte: 1 M KOH aqueous solution. Related to Figure 5.
Figure S10. I-t curves of P-TiO$_2$/Ni(OH)$_2$ under illumination at different potentials under illumination. Light source: AM 1.5 G sunlight simulator, Electrolyte: 1 M KOH aqueous solution. Related to Figure 5.

Figure S11. The band diagrams of the interfaces between FTO/Fe$_2$O$_3$/Ni(OH)$_2$ and FTO/TiO$_2$/Ni(OH)$_2$ without applied potential. Related to Figure 5.

Transparent Methods

Preparation of Ti-doped Fe$_2$O$_3$ nanorod films

Ti-doped Fe$_2$O$_3$ nanorod films were prepared by a hydrothermal method. Typically, the precursor solution was prepared by dissolving 0.012 mol FeCl$_3$•6H$_2$O, 0.024 mol urea and 80 µL TiCl$_3$ (15.0~20.0% TiCl$_3$ in 30% HCl) into 80 mL ultrapure water by magnetic stirring. Afterwards, the precursor solution was transferred into a 100 mL Teflon-lined stainless steel autoclave with FTO substrates in it. FeOOH films were deposited on the FTO substrates after hydrothermal reaction at 100 °C for 6 h in an electric oven, and washed with deionized water. The Ti-doped Fe$_2$O$_3$ nanorod films were obtained after the FeOOH films were calcined at 250 °C for 10 min, subsequent 550 °C for 120 min and then 650 °C for 30 min in air.

Preparation of TiO$_2$ nanorod films
TiO$_2$ nanorod films were also prepared on FTO substrates by a hydrothermal method. The precursor solution was obtained by mixing 0.45 mL titanium butoxide, 15 mL HCl and 15 mL H$_2$O. The solution was transferred to a Teflon-lined stainless steel autoclave with FTO substrates in it. After hydrothermal reaction at 150 °C for 9 h, the deposited films were rinsed by deionized water and calcined at 450 °C for 1 h in air to obtain TiO$_2$ nanorod films.

**Deposition of Ni(OH)$_2$**

Ni(OH)$_2$ was grown on Fe$_2$O$_3$ and TiO$_2$ nanorod films by chemical bath deposition method (CBD) and photoelectrodeposition (PED) method, respectively. For a CBD method, Ni(OH)$_2$ was grown on FTO, Fe$_2$O$_3$ and TiO$_2$ nanorod films in phosphate buffer solution containing 0.03M Na$_2$S$_2$O$_8$ and 0.02 M Ni(NO$_3$)$_2$$\cdot$6H$_2$O at 70 °C for 10 min. For a PED method, Ni(OH)$_2$ was photoelectron-deposited at 0.35 V vs. Hg/HgO for Fe$_2$O$_3$ and -0.15 V vs. Hg/HgO for TiO$_2$ in 0.1 M Ni(SO$_4$)$_2$$\cdot$6H$_2$O aqueous solution with pH=7.0 (adjusted by 0.1 M KOH) under front illumination, respectively. The deposition charges on Fe$_2$O$_3$ and TiO$_2$ nanorod films were both 9 mC/cm$^2$. Ni(OH)$_2$ was also grown on FTO, carbon paper substrates and Pt in 0.1 M Ni(SO$_4$)$_2$$\cdot$6H$_2$O aqueous solution with pH=7.0 (adjusted by 0.1 M KOH) by electrodeposition. The deposition potential was -0.7 V vs. Hg/HgO and the deposition charge was 70 mC/cm$^2$.

The different deposition behaviors of Ni(OH)$_2$ in C-Fe$_2$O$_3$/Ni(OH)$_2$ and P-Fe$_2$O$_3$/Ni(OH)$_2$ samples are explained as follows. A CBD method is a solution reaction process, in which Ni$^{2+}$ ions can spontaneously siege Fe$_2$O$_3$ nanorods and generate the full coverage of Ni(OH)$_2$ layer. Comparably, for a PED method, NiOOH is firstly deposited on the surface of Fe$_2$O$_3$ nanorods by photo-oxidation of Ni$^{2+}$ under front illumination, and then electrochemically reduced to Ni(OH)$_2$ in the dark. Therefore, Ni(OH)$_2$ was deposited only on the top of Fe$_2$O$_3$ nanorods as most of holes were excited there.

**Characterization of samples**

SEM (Nano Nova S230) and TEM (Tecnai G2 F20) were employed to investigate the morphologies of the samples. The depth profiles of different ions in the samples were characterized by X-ray photoelectron spectroscopy (XPS) (Thermo Scientific XPS K-alpha) using Ar ion sputter gun. The binding energies were calibrated by C 1s (284.8 eV). The loading masses of Ni(OH)$_2$ were measured by inductively coupled plasma-optical emission spectroscopy (ICP-OES).

**Electrochemical measurements**

The electrochemical and photoelectrochemical properties of the samples were investigated in a three-electrode cell. A Pt mesh and a Hg/HgO electrode were used as a counter electrode and a reference electrode, respectively. The electrochemical measurements including cyclic voltammetry (CV) curves and Galvanostatic charge-discharge (GCD) curves were both carried out on an electrochemical workstation (Chenhua, Shanghai, CHI 760E). The electrolyte was 1 M KOH aqueous solution with pH=14. A reversible hydrogen electrode (RHE) potential was obtained by the formula: E(V vs. RHE)=E(V vs. Hg/HgO) + 0.098V + 0.059×pH. The experimental and theoretical specific capacitances are calculated using Equation (1) and (2), respectively, where $Q_i$ and $Q_T$ are the experimental and theoretical specific capacitances respectively, $i$ is the discharging current density, $\Delta t$ is the discharging time, $m_{Ni(OH)2}$ is the
loading mass of Ni(OH)₂, \( M_{Ni(OH)2} \) is the relative molecular mass of Ni(OH)₂, and \( N_A \) is the Avogadro constant.

\[
Q_E = \frac{i \Delta t}{m_{Ni(OH)2}} \\
Q_T = \frac{m_{Ni(OH)2} \times N_A}{M_{Ni(OH)2} \times 6.25 \times 10^{18}}
\]

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