Direct storage of holes in ultrathin Ni(OH)2 on Fe2O3 photoelectrodes for integrated solar charging battery-type supercapacitors†

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Energy storage is a very significant issue for utilization of solar energy due to its discontinuous and unstable energy flux. Herein, for the first time, we propose a Fe2O3@Ni(OH)2 core–shell nanorod array as a photoelectrochemical battery-type supercapacitor for the direct storage of solar energy. Under light illumination, Fe2O3 absorbs solar energy and produces electron–hole pairs, while Ni(OH)2 stores the photo-generated holes, which can be released as electricity when the light is switched off. In addition, by controlling the valence band position of the semiconductor and the thickness of Ni(OH)2, the side reaction of water oxidation (electrolyte decomposition), which is harmful for the applications of a photoelectrochemical supercapacitor, can be completely suppressed. As a consequence, the specific capacitance of the Fe2O3@Ni(OH)2 photoelectrochemical supercapacitor is enhanced up to 20.6 mF cm⁻² at a discharge current density of 0.1 mA cm⁻², which is about 4.5 times that of BiVO4/PbO2 reported in a previous study. This study offers a very promising device for the direct storage of solar energy and deepens our understanding on the interface charge transfer between a photoelectrode and a battery-type capacitive material.

1. Introduction

The utilization of solar energy is a promising route to address the problems of energy shortage and environmental pollution. Solar energy storage is a very significant issue owing to its discontinuity and low density. The supercapacitors and batteries are favored both for energy storage and as output regulators.1–4 Therefore, some energy packs that combine a solar cell with a supercapacitor or a battery have been developed.5–8 In a solar cell + supercapacitor device, the solar energy is first converted into electricity, and then into chemical energy for storage (Fig. S1a†). These devices are complex and expensive.

Recently, a photoelectrochemical supercapacitor with a simple structure was proposed for solar energy conversion and storage in one step (Fig. S1b†).9–12 A concept device was constructed by depositing Ni(OH)2 battery-type capacitive material on the surface of a TiO2 photoelectrode.9 Under illumination, the TiO2 photoelectrode can absorb light to generate electron–hole pairs, which can be directly stored in the Ni(OH)2 battery-type supercapacitor material. When the light is switched off, the supercapacitor can release the stored holes as electricity. Since then, other TiO2/NiO and BiVO4/PbO2 based photoelectrochemical supercapacitors were also reported.11,12 For a conventional supercapacitor, a gas evolution side reaction that results from the decomposition of the electrolyte will harm the performance of the system.13 The water oxidation side reaction has been clearly observed on previous photoelectrochemical supercapacitors, which will lead to a low coulombic efficiency and cycle ability.10,11 Therefore, suppressing the water oxidation side reaction is highly essential to obtain a photoelectrochemical supercapacitor with high performance.

In this study, we proposed a Fe2O3@Ni(OH)2 core–shell nanorod array as a photoelectrochemical battery-type supercapacitor for the first time. We found that the water oxidation side reaction was highly sensitive to the band position of a photoelectrode and the thickness of a battery-type capacitive material. The high valence band of Fe2O3 led to a weak driving force for hole transfer from Fe2O3 to Ni(OH)2. As a result, the water oxidation side reaction could be completely inhibited when a 6 nm Ni(OH)2 shell layer was coated on a Fe2O3 array photoelectrode. After inhibiting water oxidation, the Fe2O3@Ni(OH)2 photoelectrochemical supercapacitor exhibited about 4.5-fold high area specific capacitance as that of the BiVO4/PbO2 photoelectrochemical reported supercapacitor in a previous study.
2. Experiment sections

2.1 Materials

All chemical reagents purchased were analytical grade reagents and used without further purification: FeCl₃•6H₂O (Alfa Aesar), TiCl₃ (Alfa Aesar), urea (Sinopharm), Ni(NO₃)₂•6H₂O (Beijing Chemical Works), Na₂S₂O₈ (Sigma), NaH₂PO₄•2H₂O (Sinopharm), Na₂HPO₄•12H₂O (Sinopharm), and KOH (Sinopharm).

2.2 Preparation of Ti⁺⁺ doped Fe₂O₃ films

Ti⁺⁺ doped Fe₂O₃ was prepared via a hydrothermal method following a literature procedure. Typically, 0.012 mol FeCl₃•6H₂O, 0.024 mol urea and 80 μL TiCl₃ (15.0–20.0% TiCl₃ in 30% HCl) were dissolved in 80 mL distilled water under magnetic stirring. Subsequently, the solution was transferred to a 100 mL Teflon-lined stainless steel autoclave. FTO substrates were put in the autoclave. After hydrothermal reaction at 100 °C for 6 h, the as-grown films were washed with distilled water, and then calcined at 250 °C for 10 min and 550 °C for 120 min (5 °C min) in a muffle furnace in air. Finally, Ti⁺⁺ doped Fe₂O₃ films were obtained after subsequent calcination at 650 °C for 30 min in air.

2.3 Preparation of TiO₂ films

TiO₂ films were also prepared by the hydrothermal method. FTO substrates were immersed in a Teflon-lined stainless steel autoclave containing 0.45 mL titanium butoxide, 15 mL HCl and 15 mL H₂O. Then, hydrothermal reaction was performed at 150 °C for 9 h in an electric oven. TiO₂ films were obtained after calcination at 450 °C for 1 h in air.

2.4 Coating of Ni(OH)₂ on Fe₂O₃ and TiO₂ films

Ni(OH)₂ was coated on Fe₂O₃ and TiO₂ films by the CBD method. Typically, the obtained Ti⁺⁺ doped Fe₂O₃ or TiO₂ films were immersed in a phosphate buffer solution with 0.03 M Na₂S₂O₈ and 0.02 M Ni(NO₃)₂•6H₂O. Then, the solution was heated at 70 °C for different times in an electric oven. Finally, the Ni(OH)₂-coated Fe₂O₃ and TiO₂ films were obtained.

2.5 Characterization of samples

X-ray diffraction (Rigaku Smartlab) and Raman spectroscopy (HORIBA HR800, 514 nm excitation wavelength) were performed to characterize the crystal structures. SEM (Hitachi SU-8010) and HR-TEM (JEM-2100F, JEOL) were employed to investigate the morphologies of the samples. The surface composition and valence states of the elements in the samples were characterized by XPS (PHI Quantera SXMTM). The binding energy was calibrated by C 1s (284.8 eV).

2.6 Electrochemical measurements

Electrochemical properties of the samples were measured in a three-electrode cell using an electrochemical analyzer (Chenhua CHI 660D, Shanghai). Hg/HgO and Pt mesh were used as a reference electrode and a counter electrode, respectively. The electrolyte used was 1 M KOH aqueous solution (pH = 14). RHE potential was calculated as $V_{RHE} = V_{	ext{Hg/HgO}} + 0.059pH + 0.098$. The light source used was a Xe lamp and the light intensity was 100 mW cm⁻², unless otherwise stated. Mass specific capacitances of samples were calculated from dark discharge curves using the following equation:

$$C = \frac{2i_m \int V \, dt}{\Delta V^2},$$

where $C$ (mF cm⁻²) is the specific capacitance, $i_m$ (mA cm⁻²) is the discharge current, $t$ (s) is the discharge time and $\Delta V$ is the potential window.

3. Results and discussion

3.1 Preparation and characterization of Fe₂O₃@Ni(OH)₂ nanorod array photoelectrochemical supercapacitors

According to the literature, Ti⁺⁺ doped Fe₂O₃ nanorod array films were synthesized by the hydrothermal method, followed by a modified annealing process. An Ni(OH)₂ layer was coated on the surface of Fe₂O₃ for different times (0 min, 5 min and 10 min) by the chemical bath deposition (CBD) method. The detailed procedure is given in the ESL. Fig. 1a shows the XRD patterns of bare Fe₂O₃ and Fe₂O₃@Ni(OH)₂ with the deposition time of Ni(OH)₂ for 10 min. Except for peaks of FTO substrates, two peaks at 35.5° and 64.1° are observed, which can be assigned as (100) and (300) faces of α-Fe₂O₃ according to JCPDS 33-0664. However, there were no evident XRD peaks of Ni(OH)₂ in the Fe₂O₃@Ni(OH)₂ sample, which may be due to the poor crystalline state or small amount of material. Raman spectroscopy is more sensitive to nanocrystal samples; hence, it was also performed to characterize the samples (see Fig. 1b). All of the samples show only the characteristic peaks of α-Fe₂O₃ at 219, 285, 405, 494, 601, and 1308 cm⁻¹, with no peaks of Ni(OH)₂. These results further suggest that Ni(OH)₂ is amorphous. To offer insights into the Ni(OH)₂ layer, XPS was performed to characterize Ni(OH)₂. The binding energies of Ni 2p and O 1s are shown in Fig. 1c and d, respectively. Two binding energies at about 856.6 eV and 862.8 eV are observed in the XPS map of Fe₂O₃@Ni(OH)₂ (see Fig. 1c), which are assigned to Ni²⁺. In Fig. 1d, an O²⁻ peak with an OH⁻ shoulder is observed in the XPS map of the bare α-Fe₂O₃ film. However, three peaks of 529.8 eV, 531.3 eV and 532.8 eV are observed in the XPS map of Fe₂O₃@Ni(OH)₂, which are assigned to O²⁻ species, OH⁻ group and adsorbed H₂O molecules, respectively. The intensity of the OH⁻ group in the XPS map of Fe₂O₃@Ni(OH)₂ is the strongest among the three peaks. These results suggest that there are abundant OH⁻ groups on the surface of Fe₂O₃@Ni(OH)₂. According to the abovementioned XRD, Raman and XPS data, it is concluded that amorphous Ni(OH)₂ was coated on the α-Fe₂O₃ film.

3.2 Inhibiting the side reaction of water oxidation by controlling the thickness of a Ni(OH)₂ shell layer

The morphologies of bare Fe₂O₃ and Fe₂O₃@Ni(OH)₂ with a deposition time of 10 min for Ni(OH)₂ were investigated by scanning electron microscopy (SEM). The results are shown in
Fig. S2.† Fe₂O₃ nanorods are porous and agglomerated, which results from dehydration due to the crystal phase transition from FeOOH to α-Fe₂O₃ after annealing at high temperatures.⁹ Before and after the deposition of Ni(OH)₂, the thicknesses of the two films are both about 500 nm. No evident morphology changes on Fe₂O₃ are observed, which suggests that the amount of coated Ni(OH)₂ is very small. HRTEM was used to characterize bare Fe₂O₃ and Fe₂O₃@Ni(OH)₂ with different deposition times of Ni(OH)₂, and the results are indicated in Fig. 2 and S3.† The bare Fe₂O₃ nanorod shows a smooth surface and good crystallinity. A lattice spacing of 0.267 nm is observed, which matches with the (104) plane of α-Fe₂O₃. After deposition of Ni(OH)₂ for 3 min, a thin amorphous layer is observed on the surface of the Fe₂O₃ nanorod, which is assigned to Ni(OH)₂. The Ni(OH)₂ layer plays the role of a shell wrapped around the α-Fe₂O₃ nanorod, thus forming a core–shell structure. The thickness of amorphous Ni(OH)₂ increases with the increase in deposition time. The thicknesses of Ni(OH)₂ is about 1 nm, 3.5 nm and 6 nm on Fe₂O₃@Ni(OH)₂ samples with a deposition time of Ni(OH)₂ as 3 min, 5 min and 10 min, respectively. In order to further confirm the core–shell structure of Fe₂O₃@Ni(OH)₂, we also used energy dispersive spectroscopy (EDS) mapping to characterize the samples. The results are shown in Fig. 2e. The EDS mapping confirms that Fe₂O₃ presents a hollow nanorod structure and the elements Fe, O and Ti are uniformly distributed in the nanorods. Distinct thin shell layers of Ni(OH)₂ can be observed on the surfaces of Fe₂O₃ nanorods to form core–shell structures.

Fig. 3a shows the dark current–potential curves of bare Fe₂O₃ and Fe₂O₃@Ni(OH)₂ samples with different deposition times of Ni(OH)₂ in 1 M KOH aqueous solution. For bare Fe₂O₃ (0 min), the onset potential for water oxidation is at about 1.7 V_RHE in the dark, which arises from activity of Fe₂O₃ as an OER electrocatalyst. In contrast, distinct oxidation peaks related to conversion of Ni²⁺ to Ni³⁺ (before 1.5 V_RHE) can be observed on Fe₂O₃@Ni(OH)₂ samples in the dark. The peak intensity depends on the amount of Ni(OH)₂ and increases with the increase in deposition time of Ni(OH)₂. These results suggest that the amount of Ni(OH)₂ increases with the increase in deposition time, which is in good agreement with the HRTEM images shown in Fig. 2. Moreover, Fe₂O₃@Ni(OH)₂ samples show much lower onset potentials of OER oxidation than bare Fe₂O₃ in the dark, which results from higher OER electrocatalytic activity of Ni(OH)₂.²⁹ Fig. 3b shows the photocurrent-curves of bare Fe₂O₃ and Fe₂O₃@Ni(OH)₂ samples with different deposition times of Ni(OH)₂ under illumination. Bare Fe₂O₃ exhibits high photocurrent, which results from water oxidation by photogenerated holes in Fe₂O₃.²¹,²² However, the water oxidation photocurrent decreases after deposition of Ni(OH)₂, which suggests that water oxidation on the Fe₂O₃ photoanode is inhibited after the deposition of Ni(OH)₂. Moreover, under illumination, evident peaks at about 1.0 V_RHE are observed in the current–potential curves of Fe₂O₃@Ni(OH)₂ samples (see Fig. 3b), which result from the oxidation of Ni²⁺ to Ni³⁺ by the photogenerated holes in Fe₂O₃.²³,²⁴ The intensity of oxidation peaks of Ni²⁺ to Ni³⁺ under illumination increased...
with the increase in deposition time of Ni(OH)₂. Moreover, nickel oxidation peaks at high potentials (1.4–1.5 V RHE) in the dark are still observed the current–potential curves Fe₂O₃@Ni(OH)₂ under illumination (see Fig. 3b), which suggests that Ni²⁺ can be oxidized not only electrochemically, but also photoelectrochemically. In order to further investigate the photocurrent evolving from water oxidation or Ni²⁺ oxidation, we also measured I–t curves of bare Fe₂O₃ and Fe₂O₃@Ni(OH)₂ with deposition times of Ni(OH)₂ as 5 min and 10 min under 100 mW cm⁻² illumination. The results are shown in Fig. 3c. A potential of 1.36 V RHE was selected because Ni²⁺ cannot be oxidized electrochemically at this potential in the dark, but can decouple the oxidation process of Ni²⁺ electrochemically and photoelectrochemically. All three samples show negligible current during the first 5 s, which suggests that Ni²⁺ is not oxidized at this potential in the dark. When light is switched on, a high stable photocurrent with no transient photocurrent is observed on bare Fe₂O₃. However, for Fe₂O₃@Ni(OH)₂ with a deposition time of Ni(OH)₂ as 5 min, a high transient photocurrent is generated, which then decays to a low stable photocurrent.

Fig. 2 HR-TEM images of bare Fe₂O₃ (a) and Fe₂O₃@Ni(OH)₂ with deposition time of Ni(OH)₂ as 3 min (b), 5 min (c) and 10 min (d). EDS mapping of Fe₂O₃@Ni(OH)₂ with deposition time of Ni(OH)₂ for 10 min (e).
Stable photocurrent is negligible even when the deposition time of Ni(OH)₂ is 10 min (see Fig. 3c). From previous studies, we know that the transient photocurrent evolves from Ni²⁺ oxidation by photogenerated holes in Fe₂O₃, while the stable photocurrent evolves from water oxidation. Therefore, no water oxidation happens on Fe₂O₃@Ni(OH)₂ with a deposition time of Ni(OH)₂ as 10 min. Though light intensity was increased from 100 mW cm⁻² to 300 mW cm⁻², stable photocurrent was still very low on Fe₂O₃@Ni(OH)₂ with a deposition time of Ni(OH)₂ for 10 min (see Fig. 3d), which suggests that water oxidation is completely inhibited by increasing the deposition time of Ni(OH)₂ to 10 min. LSV curves further confirm water oxidation on a Fe₂O₃@Ni(OH)₂ with a deposition time of Ni(OH)₂ as 5 min, but no water oxidation on Fe₂O₃@Ni(OH)₂ with a deposition time of Ni(OH)₂ as 10 min under illumination with different light intensities (see Fig. S4†).

In order to understand the mechanism of inhibiting water photo-oxidation on Fe₂O₃@Ni(OH)₂, a TiO₂@Ni(OH)₂ photoelectrochemical supercapacitor was also prepared as a reference, following a literature method (see Fig. S5†). Dark and photocurrent-potential curves of bare TiO₂ and TiO₂@Ni(OH)₂ with deposition times of Ni(OH)₂ as 5 and 10 min were measured. The results are shown in Fig. S6.† Different from that observed for Fe₂O₃@Ni(OH)₂, stable photocurrent of water oxidation was still clearly observed after the deposition time of Ni(OH)₂ as 10 min (see Fig. S6b†). These results suggest that a semiconductor plays a significant role in inhibiting water photo-oxidation in a photoelectrochemical supercapacitor. Band diagrams of Fe₂O₃/Ni(OH)₂ interface in the dark and under illumination are plotted in Fig. 4. In the dark, Δη₁(Eᵥb – Eᵣₑ₉ₒₓ) is the driving force for hole transfer from a semiconductor to a battery-type capacitive material. Δη₂(Eᵣₑ₉ₒₓ – Eₒₒ₋OH) is the driving force for hole transfer from a capacitive material to water. When the Fe₂O₃@Ni(OH)₂ photoelectrochemical supercapacitor is illuminated, Ni(OH)₂ is oxidized into NiOOH and Eᵣₑ₉ₒₓ of Ni(OH)₂ shifts lower to the valence band of Fe₂O₃, which decreases the value of Δη₁ and leads to considerable recombination of photogenerated electrons and holes (see Fig. 4b). Moreover, if Δη₂ is small, holes will accumulate in Ni(OH)₂ and hardly transfer to the electrolyte for water oxidation. Therefore, in order to inhibit water oxidation, both Δη₁ and Δη₂ should be small. If the thickness of Ni(OH)₂ is low, Δη₁ will decrease and Δη₂ will increase. Hence, water will be easily oxidized due to the high driving force Δη₂. If the thickness of Ni(OH)₂ is large enough, Eᵣₑ₉ₒₓ of Ni(OH)₂ will split. The Eᵣₑ₉ₒₓ of Ni(OH)₂ at the inner layer comes closer to the valence band in Fe₂O₃, while the Eᵣₑ₉ₒₓ of Ni(OH)₂ at the outer layer comes closer to the potential of water oxidation. In this case, it is possible to maintain low Δη₁ and Δη₂ at the same time (see Fig. 4c). Therefore, water oxidation can be inhibited by increasing the thickness of Ni(OH)₂. However, for a semiconductor with a deep valance band, such as TiO₂, it is very difficult to make Δη₁ and Δη₂ small at the same time. Water oxidation will still happen on a TiO₂@Ni(OH)₂ photoelectrochemical supercapacitor even after coating a much thicker Ni(OH)₂ (~50 nm) layer on the surface of TiO₂. Therefore, the water oxidation side reaction is highly sensitive to the valence band position of the semiconductor absorber and the thickness of the battery-type capacitive material.

3.3 Electrochemical performance of Fe₂O₃@Ni(OH)₂ photoelectrochemical supercapacitors

Discharge ability is also crucial for a photoelectrochemical supercapacitor. Photocapacitive properties of the samples were investigated in a three-electrode system in 1 M KOH aqueous solution. Fig. 5a shows the cyclic voltammetry curve of Fe₂O₃@Ni(OH)₂ with a deposition time of Ni(OH)₂ for 10 min in the dark and under illumination. In the dark, no evident redox peaks appear even at a high scan rate of 50 mV s⁻¹ because the potentials are not high enough to oxidize Ni²⁺ or water. However, distinct oxidation and reduction peaks are observed when Fe₂O₃@Ni(OH)₂ is illuminated, which suggests that Ni(OH)₂ ↔ NiOOH is reversible on the surface of Fe₂O₃ electrodes. The reversible process is helpful for charge-discharge performance. When scan rates increase from 5 to 50 mV s⁻¹, the current density increases along with a positive shift in the oxidation peak and negative shift in the reduction peak. The phenomena possibly occur due to electrolyte...
diffusion resistance.\textsuperscript{21,22} Fig. 5b shows the photo-charge and dark-discharge curves of bare Fe\textsubscript{2}O\textsubscript{3} and Fe\textsubscript{2}O\textsubscript{3}@Ni(OH)\textsubscript{2} with the deposition time of Ni(OH)\textsubscript{2} as 5 min and 10 min. For bare Fe\textsubscript{2}O\textsubscript{3}, the potential quickly increases to 1.1 V\textsubscript{RHE}, and then remains stable under illumination. When light is switched off, the potential quickly decreases without delay. In this case, only water is oxidized and no other reactions happen. Different from a bare Fe\textsubscript{2}O\textsubscript{3} sample, the potential of Fe\textsubscript{2}O\textsubscript{3}@Ni(OH)\textsubscript{2} with the deposition time of Ni(OH)\textsubscript{2} as 5 min quickly increases to 1.0 V\textsubscript{RHE}, and then slowly increases to 1.22 V\textsubscript{RHE} and finally remains stable. When the light is switched off, the potential decays quickly and then slowly, which suggests that the discharge process occurs in the dark. Since Ni\textsuperscript{2+} oxidation is easier than water oxidation, an initial potential of 1.0 V\textsubscript{RHE} for Fe\textsubscript{2}O\textsubscript{3}@Ni(OH)\textsubscript{2} with the deposition time of 5 min is lower than that for the bare Fe\textsubscript{2}O\textsubscript{3} photoelectrode (1.1 V\textsubscript{RHE}). During initial 20 s illumination, Ni\textsuperscript{2+} oxidation is dominant, which leads to the enhancement of potential by photocharging. However, when Ni\textsuperscript{2+} is mostly oxidized into Ni\textsuperscript{3+}, water oxidation is dominant and the potential remains stable, similar to that observed for bare Fe\textsubscript{2}O\textsubscript{3}. These results suggest that the amount of Ni\textsuperscript{2+} obtained with the deposition time for 5 min is not enough to completely inhibit water oxidation. When the deposition time of Ni(OH)\textsubscript{2} increases to 10 min, Fe\textsubscript{2}O\textsubscript{3}@Ni(OH)\textsubscript{2} exhibits a perfect photo-charge and dark-discharge curve, which is very similar to that of a conventional supercapacitor. The potential continues to increase, and no potential plateau is observed during photo-charging, which further confirms that water oxidation is completely inhibited by increasing the deposition time of Ni(OH)\textsubscript{2} to 10 min. In contrast, the potentials become saturated and distinct plateaus are observed on TiO\textsubscript{2}@Ni(OH)\textsubscript{2} with different deposition times of Ni(OH)\textsubscript{2} during photo-charging (see Fig. S7†). These results further confirm that water oxidation cannot be completely inhibited by increasing the deposition time of Ni(OH)\textsubscript{2} on a TiO\textsubscript{2} photoelectrode.

As shown in Fig. 5c, the open-circuit potential of Fe\textsubscript{2}O\textsubscript{3}@Ni(OH)\textsubscript{2} samples with different deposition times of Ni(OH)\textsubscript{2} show different initial \( V_{oc} \) and decay rates. The higher \( V_{oc} \) suggests more holes stored in the Fe\textsubscript{2}O\textsubscript{3}@Ni(OH)\textsubscript{2} electrode after light charging. The decay in \( V_{oc} \) results from the consumption of holes by the water oxidation side reaction. Moreover, since the consumption rate of holes is faster, the decay rate of \( V_{oc} \) is faster.\textsuperscript{27} These results further confirm the significance of the inhibition of the water oxidation reaction. Since Fe\textsubscript{2}O\textsubscript{3}@Ni(OH)\textsubscript{2} with the deposition time of Ni(OH)\textsubscript{2} as 10 min is the best sample for a photoelectrochemical supercapacitor, specific capacitance of Fe\textsubscript{2}O\textsubscript{3}@Ni(OH)\textsubscript{2} with the deposition time of Ni(OH)\textsubscript{2} as 10 min was measured. The results are shown in Fig. 5d. Fe\textsubscript{2}O\textsubscript{3}@Ni(OH)\textsubscript{2} shows negligible capacitance at the same potential window in the dark (see Fig. S8†), which suggests that stored energy in Fe\textsubscript{2}O\textsubscript{3}@Ni(OH)\textsubscript{2} is generated from light and not electricity. Different from a conventional supercapacitor, specific capacitance of a photoelectrochemical
supercapacitor depends on photo-charge time (see Fig. S9†). Therefore, in this study, photo-charge curves were measured with the same charge time. To exclude the effect of oxygen reduction reaction on the capacitance, dark discharge curves of Fe₂O₃@Ni(OH)₂ with the deposition time of Ni(OH)₂ as 10 min were also tested in air, oxygen and nitrogen (see Fig. S10†). Discharge curves in the three different atmospheres are similar, which suggest that no oxygen reduction but only Ni³⁺ reduction happens during the dark discharge process. Moreover, bare Fe₂O₃ exhibits negligible capacitance during the dark charge process (see Fig. 5b). Therefore, only Ni(OH)₂ is a capacitive active material.

The loading mass of Fe₂O₃ and Ni(OH)₂ in Fe₂O₃@Ni(OH)₂ with a deposition time of Ni(OH)₂ as 10 min was measured as about 156.6 μg cm⁻² and 9.5 μg cm⁻², respectively, by inductively coupled plasma-optical emission spectroscopy (ICP-OES). Specific area capacitance of the sample decreases from 14.0 to 20.6 mF cm⁻² when the discharge current density increases from 0.1 to 1 mA cm⁻². This trend is similar to that observed for a conventional supercapacitor.† We also compared the area specific capacitance of our sample with that of the BiVO₄/PbO₂ photoelectrochemical supercapacitor as well as other PV-supercapacitors in Table S1.† The area specific capacitance of our sample is about 4.5-fold higher than that of the BiVO₄/PbO₂ photoelectrochemical supercapacitor reported previously. The thickness of the capacitive material is significant to specific capacitance of a photoelectrochemical supercapacitor, which is only about 6 nm in this study and much less than the thickness of Ni(OH)₂ capacitive materials on TiO₂ in previous reports (50 nm).† Moreover, in the TiO₂@Ni(OH)₂ photoelectrochemical supercapacitor, high current of water oxidation during the photo-charging process leads to low coulombic efficiency (~25%). However, for a Fe₂O₃@Ni(OH)₂ sample with 10 min deposition time of Ni(OH)₂, the coulombic efficiency is about 78% at 0.1 mA cm⁻², as shown in Fig. 5d. Cycling capability is another important parameter for application of a photoelectrochemical supercapacitor. Fig. S11† indicates the cycling capability of Fe₂O₃@Ni(OH)₂ with a deposition time of Ni(OH)₂ for 10 min. The specific capacitance is maintained at about 66% after the 1000 cycles’ test.

A schematic of photo-charge and dark-charge processes on Fe₂O₃@Ni(OH)₂ with different thickness is plotted in Fig. 6. In the photocharge process, if the Ni(OH)₂ layer thickness is 3.5 nm, it is oxidized to NiOOH by photogenerated holes in Fe₂O₃ and then, water is oxidized into oxygen. In contrast, if Ni(OH)₂ layer thickness is 6 nm, diffusion lengths of the holes in Ni(OH)₂ are limited due to small driving force at the interface between Fe₂O₃ and Ni(OH)₂. Hence, only the inner layer of Ni(OH)₂ is oxidized to NiOOH by photogenerated holes. The outer layer is still Ni(OH)₂ since it has a small driving force for holes to oxidize water. Therefore, water oxidation reaction is completely inhibited. In the dark discharge process, 3.5 nm NiOOH releases holes into Fe₂O₃ and transforms back to Ni(OH)₂. However, a side reaction of water oxidation is irreversible and leads to the loss of photogenerated holes. For a 6 nm Ni(OH)₂ coated Fe₂O₃, no irreversible reactions occur and all the photogenerated holes are released into Ni(OH)₂. Therefore, a high specific capacitance and cycling capability is obtained in a 6 nm Ni(OH)₂ coated Fe₂O₃ photoelectrochemical supercapacitor.

4. Conclusions

In summary, a Fe₂O₃@Ni(OH)₂ core–shell nanorod array film was used as a photoelectrochemical supercapacitor for the first time. We found that the water oxidation side reaction sensitively depended on the valence band position of the core photoanode and the thickness of the shell layer. Different from the TiO₂@Ni(OH)₂ photoelectrochemical supercapacitor, water oxidation on the Fe₂O₃@Ni(OH)₂ photoelectrochemical supercapacitor decreased with the increase in the thickness of the Ni(OH)₂ shell layer, and was completely inhibited when the thickness of the Ni(OH)₂ layer was only 6 nm. By inhibiting water oxidation, the Fe₂O₃@Ni(OH)₂ photoelectrochemical battery-type supercapacitor exhibited a specific capacitance of 20.6 mF cm⁻² at a discharge current density of 0.1 mA cm⁻²,
which was about 4.5 times as high as that of BiVO$_4$/PbO$_2$ reported in a previous study. These results show a great potential of the novel Fe$_2$O$_3$@Ni(OH)$_2$ photoelectrochemical supercapacitor in solar energy conversion and storage.

**Author contributions**

W. Luo proposed the concept and designed the experiment. K. Zhu prepared the samples and measured the electrochemical properties. G. Zhu and J. Wang characterized the samples. J. Zhu and G. Sun analysed electrochemical data. W. Luo and K. Zhu wrote the manuscript. All authors discussed the results and commented on the manuscript.

**Conflicts of interest**

There are no conflicts to declare.

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