Integrated photoelectrochemical energy storage: solar hydrogen generation and supercapacitor

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Current solar energy harvest and storage are so far realized by independent technologies (such as solar cell and batteries), by which only a fraction of solar energy is utilized. It is highly desirable to improve the utilization efficiency of solar energy. Here, we construct an integrated photoelectrochemical device with simultaneous supercapacitor and hydrogen evolution functions based on TiO2/transition metal hydroxides/oxides core/shell nanorod arrays. The feasibility of solar-driven pseudocapacitance is clearly demonstrated, and the charge/discharge is indicated by reversible color changes (photochromism). In such an integrated device, the photogenerated electrons are utilized for H2 generation and holes for pseudocapacitive charging, so that both the reductive and oxidative energies are captured and converted. Specific capacitances of 482 F g⁻¹ at 0.5 A g⁻¹ and 287 F g⁻¹ at 1 A g⁻¹ are obtained with TiO2/Ni(OH)2 nanorod arrays. This study provides a new research strategy for integrated pseudocapacitor and solar energy application.

Solar energy offers a clean, abundant and unlimited energy resource to mankind and provides a green way to fulfill the global demand for carbon-free energy1. The sunlight provides us with a wide spectrum of applications such as solar heating2, photovoltaics3, photoelectrochemical water splitting4–6, photosynthesis7, and photocatalysis8–10. However, these solar energy harvest and storage strategies are so far developed as independent technologies. For example, considerable research efforts are being dedicated to TiO2, but they are mostly specified to only one type of solar energy capture, either the oxidative or reductive energy11–18. More efficient harnessing of the sunlight potential still remains a challenge, which requires new materials or device design.

Among various power sources, supercapacitors have attracted increasing attention over the last decade due to their high power performance, fast recharge capability, and low maintenance cost19–21. While solar-driven supercapacitors are still far from practical applications, the related research is emerging. Recently, Halls et al developed a photogalvanic cells based on lyotropic liquid crystal nanosystems doped by photoactive molecules and showed promise for application as an electrochemical capacitor22. To date, pseudocapacitive metal hydroxides and oxides are being explored for producing supercapacitors with increased specific capacitances and high energy densities23–26. There is little literature on solar-driven supercapacitors based on hydroxides and oxides. This is because almost all the explored pseudocapacitive hydroxides and oxides are not photosensitive under natural sunlight illumination and thus cannot directly capture the solar energy. An effective way is to couple them with photosensitive semiconductor materials, such as TiO2, WO3 and MoO3. The photogenerated electrons and holes, when rationally separated from their exciton state, can drive the reduction and oxidation reactions, respectively27. More specifically, the oxidative energy obtained from light-irradiated semiconductors can be stored in pseudocapacitive materials by electrochemical reactions. Simultaneously, the photoelectrons (reductive energy) can be stored in H2 via solar light-driven water splitting, or for anti-corrosion28 and bactericidal effects29. Furthermore, most of the pseudocapacitive materials are photochromic, namely, their optical transmission property depends on the charge state. Therefore, this photochromism phenomenon can be used to as an indicator of the solar energy storage within the pseudocapacitive materials.

Based on above considerations, here we report a concept device where both oxidative and reductive energies are effectively utilized by a single electrode. Our concept is illustrated schematically in Fig. 1a. The core components in this device are TiO2-based core/shell heterostructured nanorod arrays, in which the shell materials are...
shell nanorods such as TiO2/Ni(OH)2, TiO2/Co(OH)2 and TiO2/
ination or electrodeposition (see schematics in Fig. 1b). Several core/
glass, followed by coating of shell materials by chemical bath depos-
energy electrochemically.

The quasi-alignment of the TiO2 nanorods is desirable for the sub-
as shown by scanning electron microscopy (SEM) images in Fig. S1. The nanorods have diameters around 100 nm and lengths up to 1.5

Results

The TiO2 nanorod arrays are first hydrothermally grown on FTO
glass, followed by coating of shell materials by chemical bath depos-
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The corresponding reaction on the Pt electrode is 2H2O + 2e− → H2 + 2OH−. Therefore, with this new strategy, it is possible to store solar energy electrochemically.

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ligible currents. Therefore, it is concluded that 0.4 V is an appropri-
ate potential bias for the TiO2/Ni(OH)2 system.

To realize the oxidation of pseudocapacitive materials by photo-
generated holes, a reasonable potential bias needs to be selected, so that it only activates the separation of the photogenerated charge carriers but does not cause extra electrochemical reactions. Figure 3a shows the cyclic voltammetry (CV) curves of the TiO2 nanorod and TiO2/Ni(OH)2 core/shell nanorod arrays under the dark condition. The signal of the TiO2 nanorod array is negligible. For the core/shell array, when the potential is higher than 0.4 V (vs. Ag/AgCl), intrinsic electrochemical reaction of the redox couple Ni(OH)2/NiOOH occurs. Therefore, in order to avoid the interfer-
ence of this reaction, we select 0.4 V as the potential bias for the purpose of electron-hole pair separation in the photoelectrochemical process (see below).

To characterize the photoelectrochemical property of the inte-
grated anode, linear sweep voltammograms (LSV) are recorded both in the dark and under simulated solar light illumination condition to show the J−V curves (Fig. 3b). The TiO2/Ni(OH)2 nanorod arrays present a current density of 0.45 mA cm−2 at 0.4 V (vs. Ag/AgCl), slightly lower than pure TiO2 nanorod arrays (0.52 mA cm−2). Both samples show negligible dark current signals. This indicates that the core/shell nanorod arrays can effectively separate the photogenerated electron-hole pairs at 0.4 V bias while the intrinsic electrochemical reaction of Ni(OH)2/NiOOH is not triggered. To double check if the potential bias at 0.4 V is reasonable, we further compare the current-time response under different potential biases. The photo-
current under 0.4 V bias under light illumination is higher than those under 0.35 V and 0.3 V (Fig. 3c), implying that a higher potential bias is more effective in separating the photogenerated carriers. Without light illumination, all potential biases produce only neg-
ligible currents. Therefore, it is concluded that 0.4 V is an appropri-
ate potential for the TiO2/Ni(OH)2 system.

Under light illumination at 0.4 V bias for 300 s, the oxidation of Ni(OH)2 to NiOOH by the photogenerated holes can be manifested by a color change from ivory-white to brown dark (see photographs in Fig. 3d). The photochromism phenomenon is revealed also by the diffuse reflectance spectra (see Fig. 3d). After light illumination, the reflectance of the photoanode significantly lowers due to the strong absorbance of NiOOH. The oxidative energy storage is proven by potential-time response under light illumination (Fig. 3e). Without light illumination, the potential of the photoanode is around 0.3 V. Without light illumination, the potential quickly increases to 0.35 V and approaches 0.4 V. The post-illumination open-circuit potential maintains at around 0.3 V, indicating that part of the oxid-
ative energy has been stored (Fig. 3f). The potential increase has been also demonstrated in Ni/MH batteries that the potential of the nickel hydroxide electrode will increases over 0.3 V when Ni(OH)2 is electrochemically oxidized. In contrast, under the dark...
condition the potential quickly drops to about $-0.15$ V (Fig. 3f).

This implies no energy has been captured and stored even at the applied potential. The oxidative energy storage and phase change are also confirmed by the X-ray photoelectron spectroscopy (XPS) results (see details in Fig. S5).

The stored oxidative energy is now used for charging a supercapacitor, an electrochemical energy storage device required to provide high power while maintaining its energy density (or specific capacitance) at a high charge/discharge rate. The charge is performed at 0.4 V bias for 300 s under light illumination. The supercapacitor properties are tested by galvanostatic discharge at different current densities. Discharge curves of the TiO$_2$/Ni(OH)$_2$ core/shell nanorod arrays and the corresponding specific capacitance values are shown in Fig. 4a and b, respectively. Although the rate capability is not satisfactory at this stage, the specific capacitance obtained at a low current density ($482$ F g$^{-1}$ at 0.5 A g$^{-1}$) by the solar charging is comparable to typical oxide films such as NiO and Co$_3$O$_4$ driven by electrical charging$^{30-32}$. The solar-to-pseudocapacitance efficiency ($\eta$) of the TiO$_2$/Ni(OH)$_2$ core/shell nanorod arrays is calculated to be $\sim 0.2\%$ (see experimental in detail). The efficiency is not high mainly due to the relatively low incident-photon-to-carrier conversion efficiency of the TiO$_2$ host.

Strikingly, Nyquist plots reveal that the electrochemical impedance of the photoanode dramatically decreases to a very low level due to the formation of NiOOH (n-type semiconductor) by photooxidation (Fig. S6a). After discharge, the impedance returns to the high value due to the back reaction to Ni(OH)$_2$ (p-type semiconductor) (Fig. S6b). Moreover, the overall porous structure, particularly the flakey branches, can provide large active surface areas ($198$ m$^2$ g$^{-1}$, see Fig. S7) and thus short diffusion paths for both electrons and ions, which is beneficial to high capacitances. The effect of light illumination time on the capacitance is shown in Fig. 4c. One can see that $300$ s is a reasonable time to complete the solar charging. In the composite core/shell nanorod arrays, the pure TiO$_2$ nanorods contribute little to capacitance. All released energy originates from the NiOOH $\rightarrow$ Ni(OH)$_2$ conversion with simultaneous reversed color changes from dark to light brown (Fig. 4d). This means the photochromism is reversible in parallel with the charge/discharge cycles. In contrast, without light illumination no discharge behavior can be observed under the same test condition. It is noticed that the TiO$_2$/Ni(OH)$_2$ core/shell nanorod arrays also show color change to light brown under light illumination at open circuit potential without potential bias, but the potential is very low (below $-0.2$ V). Under this condition, no energy release can be observed even after light illumination for 30 min.

Similar solar electrochemical charging is also demonstrated in TiO$_2$/NiO (Fig. S8) and TiO$_2$/Co(OH)$_2$ (Fig. S9) core/shell nanorod arrays, except for lower charge separation efficiencies and specific capacitances in these systems compared to TiO$_2$/Ni(OH)$_2$. The TiO$_2$/NiO core/shell nanorod arrays turn to brown after photooxidation and present a specific capacitance of $133$ F g$^{-1}$ at 0.5 A g$^{-1}$ and $56$ F g$^{-1}$ at 1 A g$^{-1}$, respectively. As for the TiO$_2$/Co(OH)$_2$ sample, a specific capacitance of $337$ F g$^{-1}$ at 0.5 A g$^{-1}$ is observed with distinct color change from pale green to brown after the charging. The potential bias is dependent on the intrinsic potential of corresponding redox couple. For example, the potential bias for the flakey branches, can provide large active surface areas ($198$ m$^2$ g$^{-1}$, see Fig. S7) and thus short diffusion paths for both electrons and ions, which is beneficial to high capacitances. The effect of light illumination time on the capacitance is shown in Fig. 4c. One can see that $300$ s is a reasonable time to complete the solar charging. In the composite core/shell nanorod arrays, the pure TiO$_2$ nanorods contribute little to capacitance. All released energy originates from the NiOOH $\rightarrow$ Ni(OH)$_2$ conversion with simultaneous reversed color changes from dark to light brown (Fig. 4d). This means the photochromism is reversible in parallel with the charge/discharge cycles. In contrast, without light illumination no discharge behavior can be observed under the same test condition. It is noticed that the TiO$_2$/Ni(OH)$_2$ core/shell nanorod arrays also show color change to light brown under light illumination at open circuit potential without potential bias, but the potential is very low (below $-0.2$ V). Under this condition, no energy release can be observed even after light illumination for 30 min.

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TiO$_2$/Co(OH)$_2$ is 0.1 V, lower than those of the TiO$_2$/Ni(OH)$_2$ and TiO$_2$/NiO (~0.4 V). This is understandable as the intrinsic potential of redox couple for Co(OH)$_2$/CoOOH is ~0.25 V lower than those of Ni(OH)$_2$/NiOOH and NiO/NiOOH.

**Discussion**

For a semiconductor to harvest and convert solar energy, it is necessary that, upon light irradiation, the photo-generated electrons and holes are efficiently dissociated. TiO$_2$ is an n-type semiconductor in which the electrons in the conduction band are more mobile than holes in the valence band. Hence, the oxidative energy is much more difficult to capture and store than the reductive energy. In our experiment, we utilize the oxidative energy to charge pseudocapacitive materials for supercapacitor application. This design provides several unique features: (i) the pseudocapacitive materials (transition metal hydroxides and oxides) are charged by reacting with...
photogenerated holes; (ii) the pseudocapacitive materials are also photochromics so that the energy storage and release can be monitored by the color change; (iii) the reductive energy is directly used for \( \text{H}_2 \) evolution at the Pt electrode via sacrificial water splitting. The generated \( \text{H}_2 \) can be externally stored or used for fuel cells. It is optimistic that such concept could be further improved if appropriate pseudocapacitive materials are selected to couple with TiO\(_2\) (or other solar sensitive semiconductors such as Fe\(_2\)O\(_3\) and WO\(_3\)). Alternatively, the Pt cathode could be replaced by metal hydrides (MH) such as AB\(_5\) alloys (LaNi\(_5\) type), which are commercial negative materials for Ni/MH rechargeable batteries. In this way, the AB\(_5\) alloys can store the reductive energy by capturing electrons via \[ \text{2H}_2 \overset{1}{\rightarrow} \text{2e}^{-} \text{R} \text{H}_2 \text{1} \text{2OH} \text{2} \text{R} \text{MHx} (M \text{ represents metal}) \text{33}, \text{ so that the charged photoanode and the MH alloys can complete the circuit to release the energy.} \]

In summary, a unique photoelectrochemical device with integrated functions of supercapacitor, hydrogen evolution and photochromics is developed for an improved utilization of solar energy. The feasibility of solar pseudocapacitor charging is demonstrated using TiO\(_2\)/Ni(OH)\(_2\) core/shell nanorod arrays. As an example, the solar-driven pseudocapacitor based on the TiO\(_2\)/Ni(OH)\(_2\) core/shell nanorod arrays exhibits good specific capacitance values of 482 F g\(^{-1}\) at 0.5 A g\(^{-1}\) and 287 F g\(^{-1}\) at 1 A g\(^{-1}\), respectively. With further optimization, it is optimistic that such integrated devices can have performance comparable to the electrically-charged supercapacitors.

**Methods**

**Synthesis of self-supported TiO\(_2\)/Ni(OH)\(_2\) and TiO\(_2\)/NiO core/shell nanorod arrays.** Firstly, self-supported TiO\(_2\) nanorod arrays on transparent conductive fluorine-doped tin oxide (FTO) were prepared by a facile hydrothermal synthesis method. In a typical process, the FTO substrates were first cleaned with acetone, ethanol, and deionized water for 5 min, respectively, and then dried by N\(_2\) stream. The precursor was prepared by adding 0.45 mL of titanium butoxide to a well-mixed solution containing 15 mL of HCl and 15 mL of H\(_2\)O, and then the whole mixture was stirred for another 10 min until the solution became clear. Afterward, the precursor was poured into a Teflon-liner stainless steel autoclave with the FTO substrates placed at an angle against the wall with the conductive side facing down. Hydrothermal growth was conducted at 150 °C for 9 h in an electric oven. Afterward, the FTO substrates were rinsed with deionized water and annealed at 450 °C for 1 h in ambient air. Then, the self-supported TiO\(_2\) nanorod arrays were used as the scaffold for Ni(OH)\(_2\) and NiO nanoflake growth through a simple chemical bath deposition. In our case, the parameters for chemical bath deposition should be precisely controlled in order to form core/shell structures. TiO\(_2\) nanorod arrays on FTO (masked with polyimide tape to prevent deposition on the back sides) were placed vertically in a 100 ml pyrex beaker. Solution for chemical bath deposition (CBD) was prepared by adding 0.45 mL of titanium butoxide to a well-mixed solution containing 15 mL of HCl and 15 mL of H\(_2\)O, and then the whole mixture was stirred for another 10 min until the solution became clear. Afterward, the precursor was poured into a Teflon-liner stainless steel autoclave with the FTO substrates placed at an angle against the wall with the conductive side facing down. Hydrothermal growth was conducted at 150 °C for 9 h in an electric oven. Afterward, the FTO substrates were rinsed with deionized water and annealed at 450 °C for 1 h in ambient air. Then, the self-supported TiO\(_2\) nanorod arrays were used as the scaffold for Ni(OH)\(_2\) and NiO nanoflake growth through a simple chemical bath deposition. In our case, the parameters for chemical bath deposition should be precisely controlled in order to form core/shell structures. TiO\(_2\) nanorod arrays on FTO (masked with polyimide tape to prevent deposition on the back sides) were placed vertically in a 100 ml pyrex beaker. Solution for chemical bath deposition (CBD) was prepared by adding 0.3 ml of aqueous ammonia (25–28%) to the mixture of 70 ml of 0.3 g nickel sulfate and 0.06 g potassium persulfate. Immersing into the stirring CBD solution for 6 min at 25 °C, the substrates were taken off and rinsed with distilled water. The samples were annealed at 200 °C and 300 °C in argon for 1.5 h to form TiO\(_2\)/Ni(OH)\(_2\) and TiO\(_2\)/NiO core/shell nanorod arrays, respectively. The load...
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Author contributions

X.H.X., J.S.L. and H.J.F. conceived the experiment. X.H.X. and J.S.L. fabricated the samples. C.G. contributed Fig. 1. X.H.X. and H.J.F. wrote the manuscript. H.J.F. supervised the project. All authors reviewed the manuscript.

Additional information

Supplementary information accompanies this paper at http://www.nature.com/scientificreports/

Competing financial interests: The authors declare no competing financial interests.

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