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A hexagonal nanocone array of FTO, a transparent conducting oxide, is excellent in trapping light and in photoelectrochemical water splitting.
Three-dimensional Hexagonal Fluorine-doped Tin Oxide Nanocone Array: A Superior Light Harvesting Electrode for High Performance Photoelectrochemical Water Splitting

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Photonic nanostructures hold great promise in promoting light harvesting. Here we report the first design and construction of a three-dimensional (3D) hexagonal nanocone array of fluorine-doped tin oxide (FTO) on glass as an excellent electrode for photoelectrochemical (PEC) water splitting. The PEC current density with suitably deposited Ti-doped hematite at 1.23 V vs reversible hydrogen electrode (RHE) was increased by 86% to 2.24 mA cm$^{-2}$ compared to that with the planar counterpart, mainly ascribable to the special light harvesting effect and electrode surface area provided by 3D FTO. Upon the embedment of a gold layer to concentrate the incident light to the hematite layer and the deposition of the Co-Pi catalyst with a modified procedure, the photocurrent experienced a large cathodic shift of onset potential by 360 mV and soared to a high value of 3.39 ± 0.01 mA cm$^{-2}$ (at 1.23 V), yielding a power conversion efficiency of 0.70% at a potential as low as 0.88 V vs RHE.

Introduction

Solar energy is an inexhaustible natural resource and a common dream has been to convert it efficiently into the strategically important energy form of clean fuels such as hydrogen. Since the first demonstration of O$_2$/H$_2$ generation from water photoelectrolysis by illuminating on a TiO$_2$ electrode,¹ a host of metal oxides have been explored for the photoelectrochemical (PEC) water splitting,²-¹⁶ among which the hematite, i.e., α-Fe$_2$O$_3$, is particularly promising as a photoanode material not only because of its abundance in the earth’s crust (6.3% by weight) but also due to its suitable band gap (~2.1 eV) and excellent chemical stability.¹⁷-²⁴ However, the poor majority carrier conductivity²⁵, ²⁶ and the extremely short diffusion length (less than 10 nm) of minority carriers²⁷ hold back its practical application. To overcome the limitations, extensive work has been done to customize nanostructured morphologies of hematite, together with elemental doping and catalyst deposition.²⁸-³² In 2010, Grätzel et al. developed a champion nanostructure of hematite by the atmospheric pressure chemical vapour deposition (APCVD) method, which achieved a PEC photocurrent density of 3.3 mA cm$^{-2}$ at 1.23 V vs RHE.³³

In spite of these achievements, most of the research activities in the past have been focused on the nanoscale morphology of the PEC active materials themselves and less attention has been paid to 3D ordered nanostructures. Studies have revealed that a well-designed spatially ordered 3D structure can not only enlarge the specific surface area but also “trap” the incident light to the near-surface region for enhancing light absorption.³⁴-³⁶ For some narrow band gap semiconductors with short electron diffusion lengths such as Fe$_2$O$_3$, enhancing near-surface light absorption represents a significant issue. Kim et al. utilized the lithography technique - one of the most popular nanofabrication techniques - to pattern spatially tuneable Fe$_2$O$_3$ nanobeams for PEC water splitting.⁴⁰ But this method posed stringent requirements on the materials and substrate choices, not to mention the complexity and cost of the whole process.

To overcome the problem, template-assisted methods have been brought in to engineer well-ordered 3D nanostructures, in which anodic aluminium oxide (AAO) has been a workhorse.⁴⁷ With a specially designed anodization process, the grown AAO
template could be used to construct a 3D structure with unique light trapping effects. Fan et al. developed a series of AAO templates and thus regular 3D nanostructures with special optical properties and light trapping effects, such as nanospike array, nanocone array, nanowell array, and nanopillar array.\textsuperscript{38-42}

To transfer the AAO template pattern onto another substrate, organic materials such as PDMS are often used because of their flexibility and ease of lift-off. Unfortunately, the obtained organic 3D substrates are not electrically-conductive and are unstable in high temperature environments, which largely limited their applications. In principle, one could grow the target materials directly on the AAO template, but the following chemical etching procedure may cause unexpected damage to the active materials. Although the Al nanospike array recently reported by us could be used as a 3D substrate even at high temperatures,\textsuperscript{43} their instability in either acidic or basic chemical environments remains a challenge for long term applications, not to mention the complexity and cost of additional procedures to prepare Pt/Ti/FTO protection layers. Most recently, Lin et al. reported light-trapping 3D inverted cone arrays of Al\textsubscript{2}O\textsubscript{3} for photovoltaics.\textsuperscript{44} The inverted cone architecture only permitted the trapping of incident light to near the bottom region of the structure. Leung et al. surveyed a variety of 3D nanostructures for light management for optoelectronic devices, but complications were often involved as to how to concisely incorporate the active materials.\textsuperscript{45} Up to the present, ordered nanocone arrays of transparent, conducting materials in a broad range of chemically and thermally harsh environments. More importantly, the specially designed 3D distribution provides larger electrode surface area and/or stronger light-trapping compared with the commonly used planar FTO glass substrate. In the present work, we chose hematite as the active material for demonstrating the use of the 3D ordered FTO array in PEC water splitting. The 3D FTO nanocone array as a supporting electrode is chemically stable and heat proof, permitting the use of the ultrasonic spray pyrolysis (USP) method to deposit active materials in a broad range of chemically and thermally harsh environments. More importantly, the specially designed 3D distribution provides larger electrode surface area and/or stronger light-trapping compared with the commonly used planar FTO glass substrate. In the present work, we chose hematite as the active material for demonstrating the use of the 3D ordered FTO array in PEC water splitting. Systematic optimization of the experimental conditions, including the embedment of a gold reflection layer and the deposition of a Co-Pi catalyst, allowed us to achieve a photocurrent density of a high value of 3.39 ± 0.01 mA cm\textsuperscript{-2} at 1.23 V vs RHE and a cathodic shift of onset potential of as much as 360 mV. Finite-different-time-domain (FDTD) simulations have been performed to confirm the strong light trapping of the 3D FTO substrate and the surface light absorption enhancement brought about by the gold layer. An overall power conversion efficiency (PCE) of 0.70% was obtained at a low potential of 0.88 V vs RHE.

Results and discussion

Figure 1 Schematic design of the 3D FTO substrate. (a) procedure of coating and transferring 3D FTO layer onto glass substrate; (b)-(c) SEM images (45°-tilted view) of fabricating 3D FTO nanocone array by using anodic aluminum oxide (AAO) template. (b) as-obtained AAO template with hexagonally ordered reverse-cone shaped nanopores array; the crack in middle of the figure is created on purpose to show the depth of the cone. (c) 3D FTO nanocone array obtained by filling the nanopores in AAO template with FTO precursor (ultrasonic spray pyrolysis, USP, method) and transferring FTO layer onto glass substrate. Unlike the sharp nanospike array structure formed by Al, our 3D FTO nanocone array substrate was much easier for materials to grow and needed no further chemical protection procedure.

There are two critical steps in the template-assisted fabrication of the 3D FTO array with a high quality: 1) controlled growth of FTO in the AAO nanocone template; and 2) dependable transfer of the derived FTO layer onto a glass substrate. In the former step, it is important to have a good regulation over the USP temperature; the carrier gas flow rate and the fluorine concentration (see Experimental Section). The quality of the as-grown FTO will directly impact on the FTO layer transfer step. A low-quality FTO layer was found to be difficult for transferring to a glass substrate. The difficulty lies in the fact that FTO is a very rigid and inflexible material and is strongly combined with AAO template under the USP deposition condition. One could use some kind of glue to bind the FTO layer to the glass, but most organic binding agents are intolerant of high temperatures. Here for the first time we have demonstrated a method of transferring the FTO layer directly onto a common glass substrate without using any other binding agents. The key is to heat the system to a desired temperature at which the glass substrate is just about to melt. Then under a certain pressure, the AAO-FTO template and the softened glass
substrate could be firmly joined after cooling down to the room temperature naturally. A higher temperature may cause unexpected damage to the quality of FTO and a lower temperature could not initiate the combination.

**Figure 2** FDTD simulation results of the distribution of electric field at a wavelength of 500 nm for the planar sample (a) and 3D sample with 1.2 µm pitch (b), 1.5 µm pitch (c), 1.8 µm pitch (d), which indicated strong light harvesting effect in the 3D FTO nanocone structures and the electric field near the material surface has been obviously enhanced. The colour index at the right position of each figure reflects the magnitude of |E| at that point, which has already been normalized with that of the incident EM plane polarized wave propagating in free space. We could observe that the magnitude of incident light near the surface of 1.5 µm pitch nanocone is relatively the largest among different samples. The surface of FTO has been coated with a layer of hematite to make it closer to the real situation. The incident EM plane polarized wave is set to propagate down from Z = 2.6 µm.

The procedure for the 3D FTO deposition and transfer is illustrated in Figure 1a. Using the AAO template shown in Figure 1b, we obtained a 3D FTO nanocone array substrate (Figure 1c), which is a faithful negative replica of the template. In the ordered structure, the cones have uniformly a bottom diameter of around 1 µm and a height of 1.5 µm with a pitch of 1.5 µm. Our initial choice of these parameters was guided by the FDTD simulations. As an example, Figure 2a to 2d show the FDTD simulation results for a planar electrode and 3D electrodes with a pitch of 1.2 µm, 1.5 µm and 1.8 µm, respectively, near which the cross-sectional electric field intensity (|E|) distribution of the electromagnetic (EM) wave is mapped at 500 nm. As the distance between neighboring cones is close to the incident light wavelength, the incident light becomes diffracted and the electromagnetic wave will redistribute in the nanocone area, leading to a significant electric field enhancement around the 3D structure; in other words, the incident light has been “trapped”. Obviously, all of the 3D electrodes exhibit a much lower reflectance than the planar one, indicated by the smaller magnitude above Z = 2.0 µm, meaning that more light has been trapped in the 3D nanostructures. Also

**Figure 3** SEM images of derived hematite nanocrystals and XRD analysis. (a), SEM image of optimized undoped Fe₂O₃ on planar FTO substrate, top-view; (b), SEM image of optimized undoped Fe₂O₃ on 3D FTO substrate, 45°-tilted view. The insert figure showed one of the Fe₂O₃-coated FTO nanocone in detail. It could be observed that the deposited Fe₂O₃ nanoplates have a shape of regular hexagon oriented randomly on the surface of the substrate with an average side length of 100 nm and thickness of 30 nm. The Fe₂O₃ could be deposited uniformly onto the surface of 3D FTO nanocone array. (c), XRD pattern of the hematite thin film on planar FTO, in which the red dots represent the diffraction peaks of α-Fe₂O₃ and the purple dots indicate the diffraction peaks of FTO.
the electric field at the surface Fe₂O₃ layer has been significantly enhanced in the 3D structure, resulting in more efficient absorption by the active material. Among the three pitches, the 1.5 µm pitch we chose to study acquires the largest magnitude of |E| in the near surface region (see Figure 2b to 2d).

On the 3D nanocone arrays, hematite thin films were deposited by the USP method under different experimental conditions (ESI†, Figure S1 to S3). Results are presented for the optimized samples. Figure 3a and 3b shows SEM images of the as-deposited hematite thin films on a planar (top view) and a 3D FTO (45°-tilted view) substrate, respectively. One can see from the images that the Fe₂O₃ nanocrystals are mostly in a shape of regular hexagonal nanoplate and are randomly oriented on the substrate with an average side length of ~100 nm and thickness of ~30 nm. The thickness of the Fe₂O₃ layer was estimated to be around 90-100 nm by atomic force microscope (AFM).

![Figure 4](Image)

**Figure 4** Optical and PEC measurement results. (a), Photographs of the as-prepared Fe₂O₃/FTO electrodes. The color of hematite on the 3D FTO substrate is much darker than that on the planar one, indicating much enhanced optical absorption caused by the 3D nanocone structure. (b), UV-Vis absorption spectra of Ti-doped Fe₂O₃ thin film on planar and 3D FTO substrates, confirming the enhanced optical absorption brought about by the 3D FTO nanocone structure. (c), J-V curves of Ti-doped Fe₂O₃ on planar FTO (red curve) and 3D FTO electrodes (blue curve), showing the much higher photocurrent density of the 3D FTO substrate; The error bars show the standard deviation of the data points from 10 repeated scans. (d), Incident photon-to-current efficiency (IPCE) spectra and absorbed photon to current efficiencies (APCE) spectra of the corresponding two electrodes.

After annealing at 550°C in air for 2 h, the shape of the hematite remained unchanged. The corresponding XRD pattern of our synthesized Fe₂O₃ in Figure 3c exhibits a series of diffraction peaks, which is characteristic of the pure α-Fe₂O₃ (hematite) phase (Reference code 00-002-0915). To improve the poor majority carrier conductivity, the hematite film was doped with Ti to increase the ionized donor concentration and thus the conductivity. In order to confirm the effects of doping, we compared XRD patterns of the doped and undoped samples (ESI†, Figure S5). It can be seen that after the Ti doping, the hematite exhibits an obvious shift of the (110) diffraction peak, signaling the successful doping of the Ti element into the hematite crystal structure. Besides, the XPS spectrum of a Ti-doped hematite thin film (ESI†, Figure S6) indicates that the Ti element has been successfully doped into the crystal structure in the form of Ti(IV). We found that the Ti concentration significantly influenced the morphology of the spray-grown nanocrystals (ESI†, Figure S3). Experimental results revealed that the best doping mole fraction (Ti/Fe) is about 8.5%, whereat the sample morphology could just be preserved and the largest donor density (8.64 × 10¹⁹ cm⁻³, increased by 2 orders of magnitude from the undoped sample) could be obtained (calculated from the Mott-Schottky plots, ESI†, Figure S4).

Optical properties of the samples were measured since they are of primary importance in PEC water splitting. Photographs of the 3D FTO and the planar electrodes deposited with Ti-doped α-Fe₂O₃ are shown in Figure 4a. The first overwhelming observation is that the 3D device (the left one) is much darker than the planar device (the right one), indicating a greatly enhanced optical absorption due to the 3D array nanostructure, which has been confirmed by the UV-Vis optical absorption spectra shown in Figure 4b from measurements with an integrating sphere (ESI†, Figure S7). Indeed, the hematite coated 3D device exhibits a much better light absorption than the planar one, especially at the longer wavelengths, manifesting the strong light harvesting effect of the 3D FTO nanocone array. The smallest distance between the edges of two neighboring hematite coated nanocones is around 400-500 nm, which is comparable to the incident light wavelengths and thus reduces the diffraction effect to enhance light absorption.

Shown in Figure 4c are PEC J-V curves of the two devices. First of all, the photocurrent density with the 3D electrode is 2.24 ± 0.02 mA cm⁻² at 1.23 V vs RHE, which is 1.86 times higher than that with the planar electrode. Note that there is nearly no current in the dark for both electrodes, meaning that the conductive substrates have been well covered by the hematite and it is the hematite thin film that solely contributed to the photocurrent. The enhanced photocurrent on the 3D electrode is highly consistent with the FDTD simulation results shown in Figure 2. In addition, incident photon-to-electron conversion efficiency (IPCE) measurements were carried out on the aforementioned two electrodes at 1.23 V vs RHE from 365 nm to 600 nm, and the IPCE spectra are shown in Figure 4d (indicated by circles). Clearly, the Ti-doped Fe₂O₃ on 3D FTO substrate (blue curve) exhibits significantly enhanced quantum efficiency in the whole wavelength range, especially at > 450 nm. For example, at 500 nm, the IPCE of 19.9% for the Ti-doped Fe₂O₃ on 3D FTO substrate is much higher than that for the Ti-doped Fe₂O₃ on planar substrate (only 4.70%). This result confirms the much higher PEC performance of the 3D electrode than that of the planar electrode (Figure 4c) due to the much better utilization of the incident light. In addition, we...
calculated the absorbed photon to current efficiencies (APCE) according to the equation $\text{APCE}(\%) = \frac{\text{IPCE}(\%)}{1 - 10^{-\text{Absorbance}}}$, and the respective curves are shown in Figure 4d (indicated by triangles). Clearly, the resulting APCE values of the 3D device become close to those of the planar one especially in the long-wavelength region (e.g., > 550 nm), confirming that the improved IPCE values of the 3D device are mainly due to the light trapping effect. As mentioned above, the 3D substrate not only provides a much higher specific surface area but also imparts a light trapping effect. The PEC performance enhancement could be contributed by both the enlarged specific surface area of the 3D structure and the enhanced light harvesting due to light trapping by the 3D structure. Advantageously, the IPCE spectra could be used to deconvolute the light trapping induced enhancement and other factors such as the specific surface area.\(^{46}\) The contribution from the enlarged surface area can be estimated from the IPCE spectrum below 400 nm, since the light trapping effect may be ignored due to the much shorter wavelength than the minimum distance between the neighbouring nanocones (400-500 nm) in the 3D electrode. We found that the IPCE value at 380 nm for the Ti-doped Fe\(_2\)O\(_3\) on 3D FTO electrode is increased by 42% compared with the planar counterpart (Figure 4d), much less than the corresponding surface area increase (99% from a simple calculation). The photocurrent density increase at 1.23 V vs RHE is 86% in going from the planar to the 3D electrode, integrated over all of the wavelengths. This means that other PEC enhancement mechanisms must have contributed to the hugely enhanced light harvesting. It is worth noticing that the 42% IPCE enhancement due to the enlarged surface area from the planar to the 3D structure is in fact somewhat overestimated because there were other factors which could positively influence the performance such as light scattering. Another evidence is that at longer wavelengths of > 450 nm, the IPCE is increased by over 156%, which could ramp up to 323% at 500 nm and to 320% at 600 nm, much higher than the surface area increase as well as the photocurrent density increase at 1.23 V vs RHE. These results prove that the main contribution to the PEC performance enhancement is indeed from the strong light trapping effect in the 3D FTO array nanostructure, while the contribution from the enlarged surface area is limited.

To make full use of the FTO 3D structure with the special light harvesting property, a gold layer was introduced to further concentrate the incident light to the near surface region. The gold reflection layer was deposited right under the Fe\(_2\)O\(_3\) film by vacuum vapor deposition. Before coating hematite by USP, nanoparticle aggregates can be observed from the gold layer formed under the high-temperature deposition condition (ESI\(^+\), Figure S8). Since gold has a refractive index (smaller than 2.0 for all wavelengths in the visible region) much smaller than α-Fe\(_2\)O\(_3\) (larger than 2.6 for all wavelengths in the visible region), the incident light penetrating the α-Fe\(_2\)O\(_3\) film can be partially reflected back for secondary absorption. This is borne out by the FDTD simulation shown in Figure 5b (assuming no aggregation for simplicity). Evidently, electric field at the interface has been significantly enhanced compared with that

![Figure 5](https://example.com/figure5.png)

**Figure 5** Further enhancement of the performance of Ti-doped hematite on the champion 3D FTO electrode. (a), J-V curves of the Ti-doped Fe\(_2\)O\(_3\) on 3D FTO without gold reflection layer, with gold reflection layer and with both gold reflection layer and Co-DP\(_i\) catalyst; By using these two optimization method, we have greatly enhanced the photocurrent density at 1.23 V vs RHE from 2.24 ± 0.02 mA cm\(^{-2}\) to 2.78 ± 0.03 mA cm\(^{-2}\) (with gold layer) and to 3.39 ±0.01 mA cm\(^{-2}\) (with gold layer and Co-DP\(_i\) catalyst). The error bars on each data point show the standard deviation of the present value during 10 repeated scans. (b), FDTD simulation results of the sample with gold reflection layer at a wavelength of 500 nm, from which it could be obviously seen that the surface electric field has been greatly enhanced compared with Figure 2c. (c), Curves of PCE% of the three samples, from which we could see that compared with the bare 3D sample, a much higher PCE% (0.22%) could be obtained with a gold reflection layer, which ramp up to 0.70% at 0.88 V vs RHE when Co-DP\(_i\) catalyst has been deposited. Without the gold layer (see Figure 2c). Besides, plasmonic enhancement may also take effect if gold nanoparticle
aggregates are formed, which is evidenced from the FDTD power absorption simulations shown in ESI†, Figure S9. Experimental J-V curves in Figure 5a (green curve) have authenticated the beneficial role of the gold layer. After introducing the gold layer, photocurrent density at 1.23 V vs RHE is raised from 2.24 ± 0.02 mA cm⁻² to 2.78 ± 0.03 mA cm⁻².

To further optimize the performance of the 3D FTO array based electrodes, a Co-Pi catalyst was electrodeposited on the 3D Ti-α-Fe₂O₃/Au/FTO electrode by a modified photo-assistance method⁴⁷ (see Experimental section). Remarkably, a much higher photocurrent density of 3.39 ± 0.01 mA cm⁻² could be obtained (Figure 5a, pink curve), which is a significant improvement over the value we reported most recently (3.05 mA cm⁻²) for hematite on similar 3D Al nanospike substrate due to the double enhancements by the catalyst and gold reflection layers on top of the much lower onset potential and much larger fill factor. The significant cathodic shift of about 360 mV induced by the catalyst also makes a great contribution to the largely enhanced power conversion efficiency (PCE) (see Figure 5c), which is 0.70% at 0.88 V vs RHE. Previously a cathodic shift of onset potential larger than 350 mV was observed when Co-Pi catalyst was electrodeposited on hematite electrode,⁴⁸,⁴⁹ but the electrodeposition time was much too long (1 hour) and the as-deposited catalyst layer was thick (200 nm). By comparison, an optimized thin (tens of nanometers) layer of Co-Pi catalyst could be obtained within minutes (ESI†, Figure S10) in our case, which still provided the even larger cathodic shift of onset potential. Also we found that the performance of Co-Pi catalyst had a great dependence on the experimental condition of photo-assisted electrochemical deposition (ESI†, Figure S11), and a deposition time of 5 minutes under 200 mV bias in sodium phosphate buffer solution provided the largest cathodic shift and thus the highest photocurrent density.

Conclusions

We have for the first time succeeded in fabricating an ordered 3D FTO hexagonal nanocone array on a glass substrate by the combination of AAO templating, USP deposition and hot-transfer techniques, among which the hot-transfer step is of special importance to the materials combination involved. The fabrication process is dependable and the as-prepared 3D FTO nanocone arrays are of high quality and high performance, which could provide not only moderately enlarged surface areas but also significantly enhanced light harvesting with high stability in harsh thermal or chemical environments. By using such 3D substrates as PEC electrodes for water-splitting with properly deposited photocatalyst, Au reflection layer and cocatalyst, the photocurrent density of Ti-doped hematite has been increased from 1.32 mA cm⁻² to 2.78 mA cm⁻² and finally to 3.39 mA cm⁻² (with catalyst) at 1.23 V vs RHE. Coupled with the significantly lowered onset potential and enhanced fill factor, a conversion efficiency of 0.70% has been achieved, which represents the highest efficiency for this system measured under similar conditions. This significant improvement in the PEC performance of the hematite system indicates that the continual optimization of the 3D substrate, nanostructure, catalyst and other factors could ultimately realize the full potential of PEC water splitting.

Experimental section

Materials and Chemicals

Aluminium foil (0.25 mm thick, 99.99%, Alfa Aesar); Silicon mold; 1.2 mm thick microscope slides; Ethanol absolute (99.5%, Scharlaru); Perchloric acid (>69%, Sigma-Aldrich); Phosphoric acid (85%, VWR); Hydrochloric acid (>69%, Sigma-Aldrich); Citric acid (>99%, Fisher); Nitric Acid (68%-70%, VWR); Ethylene glycol(99.8%, Sigma-Aldrich); Tin tetrachloride pentahydrate (98%, Sigma-Aldrich); Cobalt nitrate hexahydrate (99%, Sinopharm Chemical Reagent Co., Ltd); Iron(III) chloride (99%, Riedel-dehaen); Acetylacetone (>99%, Sigma-Aldrich); Titanium disopropoxide bisacetylacetonate (75wt% in isopropanol, Sigma-Aldrich); Tetraethyl Orthosilicate (99%, RDH); Sodium Phosphate Dibasic Dihydrate (>99.5, VWR); Sodium phosphate, monobasic (>99%, Acros). All reagents were used directly without any further purification.

Synthesis of Samples

AAO Template Growth. Firstly, aluminium foil was cut into 1 cm³3 cm pieces and thoroughly cleaned in the acetone/isopropyl alcohol mixed solution under ultra-sonication for 10 min. After it was dried in compressed air, the foils were electrochemically polished in a mixture solution of perchloric acid and ethanol (1:3, v/v) for 2 minutes at 5°C. Then the polished Al foil sheets were imprinted by using the selected silicon mold with a moderate pressure. After that, the as-prepared substrates were anodized at 5°C under a direct bias of 200 V in a solution consisting of 120 ml 1 wt.% citric acid / 120 ml ethylene glycol and 1.5 ml 0.1% phosphoric acid for 30 minutes. After the first anodization, the substrates were immersed in a mixture solution of phosphoric acid (6 wt.%) and chromic acid (1.8 wt.%) at 100 °C for 5 minutes to totally etch away the first layer of AAO. The second anodization was then carried out at the same condition but with a direct bias as high as 600 V for 20 minutes. Afterward, the second etching process was conducted in 5% phosphoric acid at 53°C for 13 minutes to partially etch away some formed AAO and broaden the pore diameter. Then the same anodization and etching procedures were repeated until the fifth anodization was completed. The prepared templates were cleaned by ethanol and DI water for 3 times, respectively.

FTO Coating and Transferring. FTO precursor solution was firstly prepared by refluxing. Typically, 10.5 g SnCl₄·5H₂O was added into 150 ml absolute ethanol in a three-necked flask and refluxing for 2 hours under magnetic stirring to form uniform, stable and transparent solution. 222 mg of self-prepared NH₄F (20% by mole vs Sn) was then dissolved in 5 ml DI water and added drop by drop into the SnCl₄/ethanol solution. The refluxing system was maintained for another 3 hours, followed by cooling naturally to room temperature. Then the as-prepared AAO template substrates were cut into designed sized and pre-heated on a heating plate to 400 °C, after which the FTO precursor solution was ultrasonically sprayed onto the substrates. About 20 minutes later, a thick FTO layer was uniformly coated onto the substrates.

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Afterward, a piece of microscope slide was cut into pieces and together with the template, the glass substrates was “sandwiched” by another piece of glass at the bottom and a 200 g weight on the top (ESI†, Figure S12). The whole system was then put into a muffle furnace and heated from 25°C to 690°C in 30 minutes. Temperature was maintain at 690°C for 2 minutes, followed by program controlled cooling down to the room temperature. After heating treatment, the FTO layer was firmly stuck to the glass substrate. Then the sandwiched structure was immerssed into a mixed solution of hydrochloric acid and nitric acid at 50°C to etch away the Al foil and AAO template and a glass-supported 3D FTO nanoarray contact substrate remained.

Coating Fe$_2$O$_3$ onto 3D FTO substrate. Again we used the USP method to synthesis Fe$_2$O$_3$ thin layer. The Fe$_2$O$_3$ precursor solution was prepared as follows. We dissolved FeCl$_3$ in 29 ml DI water to obtain a 0.15 M FeCl$_3$ aqueous solution and then 1 ml of acetylacetonate was mixed with the system and the color of the solution turned from yellow to dark red immediately which indicated the formation of iron trisacetylacetonate complex. After diluted by 15 times with absolute ethanol, we obtained 0.01M iron trisacetylacetonate ethanol solution, which was then sprayed by USP method onto the 550°C 3D FTO substrate at a gas flowing rate of 1.5 L min$^{-1}$. After several minutes, the surface of the substrate would become red and a layer of Fe$_2$O$_3$ was formed with various thicknesses depending on the USP time. At last the substrate was maintained at 550°C in a Muffle furnace for 2 hours with a following naturally cooling process. For comparison purpose, we changed a series of conditions when synthesis Fe$_2$O$_3$ film, such as precursor concentration, carrier gas flowing rate and USP time, and all the details could be found in ESI†, Figure S1 to S4. The method demonstrated here was the optimized one.

Photo-assisted electrodeposition of Co-Pi catalyst. Co-Pi water oxidation catalyst was photo-assisted electrodeposited onto the 3D FTO/Fe$_2$O$_3$ device using a modified method$^{1-3}$. ENREF 47 ENREF 49. 100 ml 0.2 M phosphate buffer solution (pH = 7.0) was firstly prepared according to ESI†, Table S1. After dilute by 2 times, we got a 0.1 M buffer solution and then 13.6 mg Co(NO$_3$)$_2$.5H$_2$O was added into the solution (0.5 mM). At such a pH environment, the dissolved cobalt (II) ions would be quickly converted to Co(OH)$_2$ pink precipitate which could be clearly observed. Then hydrochloric acid was added drop by drop until the precipitate was just totally dissolved, at which point the pH of the solution was around 6.2. The prepared solution was used as electrolyte in a three-electrode PEC characterization system, and the Fe$_2$O$_3$/FTO substrate as the working electrode, a Pt net as the counter electrode, Ag/AgCl as the reference electrode. Under AM 1.5 illumination, a direct bias of 200 mV was added on the working electrode and an initial photocurrent density of ~15 µA cm$^{-2}$ was obtained. The whole photo-assisted electrodepositing process was maintained for about 5 minutes and a layer of Co-Pi catalyst was formed on the surface of the device. The catalyst was also deposited under different experimental conditions which have been elaborated on in ESI†, Figure S10.

Characterization of Samples

Morphologies of the products were examined by scanning electron microscopy (SEM; JEOL 6700F) at an accelerating voltage of 5 kV. The compositions of the products were determined by powder X-ray diffraction (XRD; Philips PW-1830) with Cu Kα radiation ($\lambda$ = 1.5406 Å) and X-ray Photoelectron Spectroscopy (XPS; Axis Ultra DLD). The optical absorption spectra were taken by a self-made UV-Vis system.

Electrochemical Measurements

All the preprepared samples were made into PEC testing devices. PEC measurements of both planar and 3D devices were conducted in a three-electrode electrochemical cell containing 1 M NaOH aqueous solution as the electrolyte, where the devices as the working electrode, a Pt net as the counter electrode and Ag/AgCl as the reference electrode. Linear-sweep voltammograms (reported with respect to the reversible hydrogen electrode (RHE), E(RHE) = E(Ag/AgCl) + 0.1976V + 0.059 pH) was recorded on different devices under 100mW cm$^{-2}$ simulated sunlight illumination. The sweeping range of the potential was from 0.5 to 1.65 V vs RHE, IPCE measurement was also conducted in the same testing system with a wavelength range from 365 nm to 600 nm.

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Notes and references

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Broader context
Sunlight harvesting is the most promising solution to the problem of sustainability facing humanity. Photoelectrochemical (PEC) water splitting rises as an important technology to produce the energy-rich and cleanest fuel --- hydrogen. Despite the various semiconductor materials that have been developed for enhancing charge separation required for splitting water, little attention has been paid to trapping light by depositing the active materials to a three-dimensional (3D) ordered, transparent and conducting substrate due to the technical difficulties involved. In the present work, we have designed and fabricated a glass-supported 3D hexagonal nanocone array of fluorine-doped tin oxide (FTO) --- a transparent and conducting material --- by combining the techniques of template assistance and hot-joining, as a superior substrate for PEC water splitting with strong light harvesting effect. Using Ti doped hematite as the photoactive material deposited by ultrasonic spray pyrolysis, we find a greatly enhanced PEC performance for the 3D FTO substrate as compared to the flat counterpart mainly due to the strong light harvesting effect. The significant advancement demonstrated here bolsters the promise of the strategies for developing 3D FTO substrates to enhance light harvesting efficiencies of PEC water splitting devices.