Cubic In$_2$O$_3$ Microparticles for Efficient Photoelectrochemical Oxygen Evolution

Ming Meng,† Xinglong Wu,*,† Xiaobin Zhu,† Lun Yang,† Zhixing Gan,† Xiaoshu Zhu,§ Lizhe Liu,† and Paul K. Chu†

†Key Laboratory of Modern Acoustics, MOE, Institute of Acoustics, Collaborative Innovation Center of Advanced Microstructures and Department of Physics, Nanjing University, Nanjing 210093, P. R. China
‡Department of Physics, NingBo University, NingBo 3153001, China
§Center for Analysis and Testing, Nanjing Normal University, Nanjing 210093, P. R. China
¶Department of Physics and Materials Science, City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong, China

Supporting Information

ABSTRACT: Cubic In$_2$O$_3$ microparticles with exposed {001} facets as well as single morphology and size are produced on a large scale on silicon with a high yield. The morphological evolution during chemical vapor deposition is investigated and the new knowledge enables precise facet cutting. The synthesized Cubic In$_2$O$_3$ microparticles possess superior photoelectrocatalytic activity and excellent chemical and structural stability in oxygen evolution reaction on account of the unique surface structure and electronic band structure of the {001} facets. Our results reveal that it is feasible to promote the photoelectrochemical water splitting efficiency of photoanode materials by controlling the growth on specific crystal facets. The technique and concept can be extended to other facet-specific materials in applications such as sensors, solar cells, and lithium batteries.

SECTION: Surfaces, Interfaces, Porous Materials, and Catalysis

Controlled growth on specific crystal facets of inorganic functional materials has spurred many promising applications in photocatalysis,‡ photoelectrochemical (PEC) water splitting,§ dye-sensitized solar cells,§ gas sensing, and lithium batteries.§ Among these applications, PEC water splitting based on oxidation-reduction at the semiconductor/electrolyte interface is of particular interest as it integrates both solar energy collection and H$_2$/O$_2$ evolution.

Crystal facets with different atomic arrangements not only offer different active sites to break chemical bonds, but also create different barriers at the semiconductor/electrolyte interface, thereby providing the opportunity to design new materials with enhanced PEC performance. In addition, it has been shown that photoexcited electrons and holes can gather on different crystal facets leading to increased separation of photogenerated electron/hole pairs. This also implies that the exposed crystal facets play an important role in the PEC properties of semiconductor photoelectrodes, and precise control of the crystal facet is crucial.

Indium oxide (In$_2$O$_3$) with a body-center-cube (bcc) structure is an ideal model photocatalyst on account of its proper band-edge position, excellent conductivity, and superior PEC stability. It is crucial to accumulate the positively charged holes on the {001} facets because the valence sub-band is originally filled, and any deviation from this full situation should cause creation of holes. Thus, it is possible that In$_2$O$_3$ cubes with only the {001} facets exposed possess significantly enhanced PEC water splitting activity. The working principle of this photoanode system is illustrated in Figure 1. In$_2$O$_3$ cubes absorb photons that cause generation of both valence band holes and conduction band electrons. Energetic electrons flow to the cathode (Pt) via the external circuit and participate in the hydrogen evolution half-reaction, whereas energetic holes accumulate on the {001} facets due to the new valence sub-band, where these holes can transfer to the adsorbed water molecules to produce oxidation reaction. When the adsorbed water molecules are dissociated into H$^+$ and OH$^-$, transfer of

Received: November 1, 2014
Accepted: November 30, 2014
holes is expected to be more efficient because the activation barrier of oxygen evolution is reduced significantly. That is, the photogenerated holes have lower activation barrier to oxidize $\cdot OH$ than directly split water. Consequently, the oxygen evolution reaction continues in concert with the sustained dynamic process of $H_2O$ adsorption and dissociation.

Truncated octahedral $In_2O_3$ microcrystals have recently been synthesized.\textsuperscript{5} Owing to the presence of the exposed $\{001\}$ facets, they exhibit higher photoelectrocatalytic activity in comparison with octahedral $In_2O_3$ microcrystals fully enclosed by the $\{111\}$ facets. Synthesis of cubic $In_2O_3$ microcrystals with the fully exposed $\{001\}$ facets is thus highly desirable to further improve the photoelectrocatalytic performance. Theoretically, cubic crystal symmetry endows $In_2O_3$ with abundant morphologies.\textsuperscript{24,25} Although nanostructured $In_2O_3$ single crystals with a larger percentage of exposed $\{001\}$ facets have been fabricated,\textsuperscript{26−29} the yield tends to be low and size is nonuniform, thereby making it difficult to study the photoactivity of different facets accurately. In addition, most importantly, the underlying mechanism of $In_2O_3$ morphological evolution is not clear, and, in fact, some reports about the effects of the synthesis parameters on morphology evolution are sometimes contradictory.\textsuperscript{30,31} In this work, we systematically investigate the morphological evolution mechanism of $In_2O_3$ microcrystals, and with the new understanding, cubic $In_2O_3$ microcrystals with a single morphology and uniform size are produced on a large scale with a high yield by a modified chemical vapor deposition (CVD) method (Figure S1 in Supporting Information). The facet-controlled $In_2O_3$ microcubes show a larger photocurrent density in PEC water splitting than those with a smaller percentage of the exposed $\{001\}$ facets and the Faraday efficiency of oxygen evolution reaction reaches 91.7%. The results provide evidence about the importance of precise and controlled facet cutting of inorganic microcrystals.

Previous reports have demonstrated that the crystal morphology of a cubic structure is dictated by the ratio ($R$) between the growth rates along the $\langle001\rangle$ and $\langle111\rangle$ directions and intrinsically determined by the surface energy of the facets.\textsuperscript{24,32} With regard to the bcc $In_2O_3$, the sequence of surface-energy ($\gamma$) for low-index crystallographic facets is $\gamma_{\{111\}} < \gamma_{\{001\}} < \gamma_{\{110\}}$, and the growth rate of the corresponding facets follow the same sequence.\textsuperscript{33} Consequently, altering the relative order of the surface energy is prerequisite to precise control of
the In$_2$O$_3$ crystal morphology. In the CVD approach, the surface energy sequence can be altered by gas-phase supersaturation related to the growth temperature.$^{28,34,35}$

A large quantity of cubic In$_2$O$_3$ microcrystals with good uniformity is fabricated by the modified CVD route at 1000 °C based on the carbothermal reduction reaction (Figure S2 in the Supporting Information). Figure 2a shows that the cubic In$_2$O$_3$ crystals have a narrow size distribution, and the average size is approximately 1 μm (Figure 2b). The inset in Figure 2b shows the magnified field-emission scanning electron microscopy (FE-SEM) image of an individual cube with smooth square facets. The shape is described by the 3D representation in Figure 2c. Figure 2d presents the X-ray diffraction (XRD) pattern of the cubic In$_2$O$_3$ crystals and standard card (JCPDS card No. 06-416). All the diffraction peaks can be indexed to the bcc structure of In$_2$O$_3$ (space group Ia$\bar{3}$m) except those from the silicon substrate (Figure S3 in the Supporting Information). Moreover, the diffraction intensity ratio of the (400) to (222) peak is much larger than that in the standard powder pattern (6.5 versus 0.3), indicating that more {001} facets are exposed. A typical SEM image and schematic model of a cubic microcrystal viewed along the [001] direction are shown in Figures 3a,b, which clearly reveal that the projection is a two-dimensional square constructed by edges of {010} and {100}. This is also verified by the low-magnification transmission electron microscopy (TEM) image (Figure 3c). The selected-area electron diffraction (SAED) pattern with a square symmetry and two sets of square crossing 0.506 nm fringes consistent with the {002} lattice spacing of bcc In$_2$O$_3$ are acquired from a same location. The results confirm that each freestanding microcrystal is a single crystal (Figure 3d,e). These crystallographic features are identical to the projected structure model of a cubic In$_2$O$_3$ microcrystal viewed from the [001] crystallographic direction (Figure 3f), providing convincing evidence that each single-crystal In$_2$O$_3$ cube is enclosed by six {001} facets.

To investigate the influence of the growth temperature on the In$_2$O$_3$ microcrystal morphology, experiments are also carried out at different temperature between 920 and 980 °C, while keeping the other experimental parameters the same. When the growth temperature is set to 980 °C, uniform truncated cubes are obtained with a high yield (Figure S4a,b in the Supporting Information). The average size is almost the same as that of the cubes. The magnified FE-SEM image shows that the truncated cube is enclosed by six (001) and eight {111} facets. When the temperature is further reduced, the morphology evolves from cuboctahedral to truncated octahedral and finally octahedral with high symmetry (Figure S4c−h in the Supporting Information). That is to say, the area ratio of the {001} to {111} surface decreases gradually as the temperature is decreased. This is further corroborated by XRD (Figure S5 in the Supporting Information). The diffraction intensity ratio of the (400) to (222) peak decreases from 6.5 for cubes to 4.5, 3.8 for truncated cubes and cuboctahedrons, respectively. In addition, the detailed TEM analysis of the truncated cubes and cuboctahedrons provides the same conclusion (Figure S6 in Supporting Information). According to the ultraviolet–visible (UV–vis) diffuse reflectance spectra acquired from the cubes, truncated cubes, and cuboctahedrons, no obvious difference is observed from the absorbance edges, and all the band gaps are estimated to be about 2.78 eV for these polyhedrons (Figure S7 in the Supporting Information).

According to the temperature-dependent vapor pressure profile (Figure S8 in the Supporting Information), it can be deduced that the gas-phase supersaturation of In$_2$O$_3$ increases gradually with temperature. To determine the relationship between the supersaturation (growth temperature) and relative growth rate of crystal facets, the growth mechanism of the cube is investigated at different stages, and the results are illustrated in Figure 4.

The CVD process of In$_2$O$_3$ includes two sequential stages: (i) formation of In$_2$O$_3$ vapor by chemical reactions occurring in the source materials (discussed in detail in the Supporting Information) and (ii) nucleation and growth of In$_2$O$_3$ nanocrystals on the silicon substrate. In the early stage, supersaturation is low and a large quantity of In$_2$O$_3$ exhibits the hexapod-like morphology due to the faster growth rate along the ⟨001⟩ direction (Figure 4a,b and Figure S9a,b). Afterward, newly arriving In$_2$O$_3$ clusters adsorb on the surface. They are not immediately incorporated into the crystal lattice but are able to diffuse on the surface. In this process, the surface diffusion rate of newly arriving clusters is determined by supersaturation.$^{36}$ As growth proceeds, supersaturation reduces the surface diffusion rate of the adsorbed In$_2$O$_3$ clusters and probability to migrate to the {001} facets with large surface energies. These hexapod-like nanocrystals have a large density of defects such as kinks, ledges, and steps, and growth on the {001} facets is hindered by the defects. When the growth rate on the ⟨001⟩ direction (defined as $\gamma_{(001)}$) is decreased to some extent and becomes comparable to that on the ⟨111⟩ direction (denoted as $\gamma_{(111)}$), the morphology of the In$_2$O$_3$ nanocrystal

---

**Figure 3.** (a) SEM image (scale bar: 500 nm) and (b) stimulated image of a cubic crystal viewed along the [001] direction. (c) Typical low-magnification TEM image of a cubic In$_2$O$_3$ microcrystal viewed along the [001] direction (scale bar: 500 nm). (d) SAED pattern along the [001] direction and (e) HR-TEM image (scale bar: 5 nm). (f) Schematic model of an ideal In$_2$O$_3$ cube enclosed by the {001} facets, projected along the [001] direction.
changes from hexapod to truncated-octahedron (Figure 4b,c and Figure S9c). With increasing supersaturation, $\gamma_{\{111\}}$ far exceeds $\gamma_{\{001\}}$, and thus more adsorbed In$_2$O$_3$ clusters are integrated into the lattice along the $\langle 111 \rangle$ direction instead of $\langle 001 \rangle$ as a result of energy conservation (Figure 4d,e).37 It is noted that some circular growth steps can be observed from the intermediate product, which stems from growth on the $\{111\}$ facets (Figure S10 in the Supporting Information). Finally, regular cubes surrounded by smooth $\{001\}$ facets form (Figure 4f). The observation indicates that the ratio ($R$) between the growth rates along the $\langle 001 \rangle$ and $\langle 111 \rangle$ directions decreases with increasing supersaturation. The higher the temperature, the higher the supersaturation, and the high temperature leads to exposure of more high-energy facets. As a result, the ratio ($R$) decreases with increasing temperature. The findings provide the crucial clue in order to understand the temperature-dependent morphological evolution. As the temperature is reduced from 1000 to $920^\circ C$, $R$ varies from 0.58 to 1.73 resulting in transformation from the cubical to octahedral morphology. This corresponds to gradual reduction of the percentage (defined as $P$) of the exposed $\{001\}$ facets as shown in Figure 4f–j.

Different gas flow rates lead to different positions of the largest supersaturation in the growth tube and thus drive the morphology evolution of microcrystals at a specific location.27,34 To demonstrate this effect, more investigation is performed, and it is found that when the flow rate is reduced to 100 sccm (standard-state cubic centimeter per minute), only slightly truncated In$_2$O$_3$ microcubes are formed under the same other reaction conditions (Figure S11 in the Supporting Information). Since the experiments used to produce these microcubes are performed at a large flow rate of 150 sccm in a small-diameter quartz tube, this results in only slightly different supersaturation along the gas flow direction. Hence, no noticeable morphology change is observed at different flow rates. This reflects that the flow rate is not the main factor here, whereas supersaturation closely related to both the growth

Figure 4. Morphological evolution of In$_2$O$_3$ microcrystals and growth progress of microcubes; scale bar: (a) 50, (b) 300, (c) 500 nm, and (d–j) 1 $\mu m$.

Figure 5. (a) Current versus voltage ($J$–$V$) curves of the polyhedral In$_2$O$_3$ microparticle photoanodes. The curves are obtained from a 1 M aqueous NaOH ($pH = 13.6$) solution under illumination (270 mW/cm$^2$). (b) Comparison of the photocurrent densities (0.22 V$_{Ag/AgCl}$) of the In$_2$O$_3$ polyhedrons. (c) Photocurrent density plots of cubic In$_2$O$_3$ microparticles displaying a photocurrent dependence on illumination power: red (240 mW/cm$^2$), blue (160 mW/cm$^2$), pale yellow (100 mW/cm$^2$). (d) Photocurrent versus time ($I$–$t$) curves of the In$_2$O$_3$ microcrystal photoanodes performed at 0.22 V$_{Ag/AgCl}$. Two sloping curves show the amounts of evolved O$_2$ calculated theoretically and detected experimentally of microcube photoelectrode, respectively; Different scales (left axis for the $I$–$t$ curves and right axis for the oxygen evolution curves) are used to elucidate the chemical and structural stabilities.
temperature and tube diameter is the primary driving force of the crystal morphology evolution. This is also the reason why we can obtain uniform microcubes at 1000 °C.

To evaluate the PEC water splitting properties of the In$_2$O$_3$ cubes, photoelectrocatalytic tests are conducted in a deaerated (purified with high purity N$_2$ (99.9995%)) three-electrode configuration (Figure S12 in the Supporting Information) employing an epoxy-sealed In$_2$O$_3$ microcrystal sample as the working electrode with an exposed area of 0.8 cm$^2$, Pt mesh as the counter electrode, Ag/AgCl (3 mol L$^{-1}$ KCl-filled) as a reference electrode, and 1 M NaOH (pH = 13.6) solution as the electrolyte. Figure 5a and Figure S13 in the Supporting Information display the current versus voltage ($J$–$V$) curves of the In$_2$O$_3$ cubes (red), truncated cubes (gray), cuboctahedrons (green), truncated cuboctahedrons (purple), octahedrons (pale yellow), and blank Si substrate (blue) under light illumination and dark conditions. All the samples exhibit an almost negligible dark current density in a potential range of −0.4 to 0.9 V vs Ag/AgCl, suggesting that the observed current stems from light absorption. Under irradiation of a Xe lamp, the photocurrent densities of the In$_2$O$_3$ cubes, truncated cubes, cuboctahedron and truncated octahedron increase sharply over the entire potential range, and no noticeable photocurrent is observed from the In$_2$O$_3$ octahedrons and Si substrate, indicating that the photoelectrocatalytic activity is improved largely on the exposed {001} facets. To further investigate the photoelectrocatalytic improvement, the photocurrent densities obtained at 0.22 V vs Ag/AgCl [1.23 V vs RHE (reversible hydrogen electrode)] are listed in Figure 5b. At 0.22 V vs Ag/AgCl, the current densities of the polyhedrons increase from octahedrons to cubes. The In$_2$O$_3$ cubes yield a maximal photocurrent density of 2.1 mA/cm$^2$, and it is 42 times the value obtained from In$_2$O$_3$ octahedrons and much larger than the photocurrent density of 0.14 mA/cm$^2$ collected from the In$_2$O$_3$ truncated octahedrons.$^5$ This demonstrates that the photocurrent in the process of PEC water splitting is proportional to the percentage of the exposed {001} facets among all the exposed facets.

To further identify the origin of the photocurrent, the power-and wavelength-dependent photocurrent responses are examined. The photocurrent density of the In$_2$O$_3$ cubes increases with input light power because of more absorbed photons (Figure 5c). Under irradiation by UV-blue light, the In$_2$O$_3$ cubes/Si substrate shows a large photocurrent response, but the response is reduced largely when irradiated with 500–700 nm light (Figure S14a-b). Since the photoexcited electron–hole pairs can still be produced by 500–700 nm irradiation for the Si substrate, the enhanced photocurrent response is not due to the Si substrate. In addition, the charge transport across the Si substrate/In$_2$O$_3$ junction is examined using the $J$–$V$ characteristics, and a similar conclusion is obtained (Figure S14c). PEC water splitting performance can also be influenced by the resistivity of the sample, and a lower resistivity usually leads to a larger photocurrent density. However, in the present case, the resistivity of the In$_2$O$_3$ cubes is 1.5 Ω·cm, which is larger than that of In$_2$O$_3$ truncated octahedrons (0.58 Ω·cm) and octahedrons (0.35 Ω·cm).$^5$ In addition, the nearly identical absorption features in all the polyhedral samples indicate that the enhanced oxygen evolution reaction (OER) of the In$_2$O$_3$ microcubes cannot be ascribed to improved solar light harvesting due to narrowing of the band gap caused by oxygen vacancies, as reported by previous investigations.$^{18,20}$ The above results imply that the superior photoelectrocatalytic performance of the cubic microcrystals is not due to modification of both the resistivity and absorption feature, but instead the surface structure. The electrochemical impedance spectroscopy data also show clearly that the In$_2$O$_3$ cubes possess a much lower hole transfer resistance from the surface than octahedrons, thus suggesting the existence of a surface state at the In$_2$O$_3$ {001} facet where holes gather (Figure S15 in the Supporting Information).$^{38–40}$ In other words, the exposed {001} facets play a decisive role in the enhanced photoelectrocatalytic activity. It is evident that the {001} facets of In$_2$O$_3$ possess far better photoelectrocatalytic properties than the {111} facets.

The chemical and structural stability against anodic photooxidation is important to photoanode materials. Figure 5d displays the photocurrent–time ($I$–$t$) curves of In$_2$O$_3$ microcrystals at a constant potential of 0.22 V vs Ag/AgCl under illumination for 150 min. The photocurrent density is very stable, and there is no sign of deterioration in the photocurrent during the entirely measured 20 h (Figure S16a in the Supporting Information). To determine whether the photocurrent stems from the OER on the In$_2$O$_3$ cube-based photoanode, the amount of oxygen evolved from the photoanode is quantified by a fluorescence sensor and calculated from the $I$–$t$ curve assuming 100% Faradaic efficiency (Figure 5d). The amount of evolved oxygen increases linearly with illumination time, suggesting that oxygen evolution is persistent during the entire 150 min of PEC water splitting, and the Faraday efficiency of OER is 91.7%. The 8.3% loss in the Faraday efficiency at 150 min may be due to gas leakage (Figure S16b in the Supporting Information), which can be improved by a better design of the gas test system.$^4$ Figure S17 shows the SEM and XRD patterns of the In$_2$O$_3$ cube-based photoanode after water splitting for 150 min. The surface morphology and crystal phase of the In$_2$O$_3$ cubes remain stable, suggesting that the cubic In$_2$O$_3$ photoanode has high stability in OER. Our results show that the good PEC water splitting characteristics rendered by the In$_2$O$_3$ cubes are due to a precise facet.

In conclusion, In$_2$O$_3$ cubes with exposed {001} facets as well as single morphology and size are produced on a large scale on silicon with a high yield. The morphological evolution during CVD is investigated, and the new knowledge enables precise facet cutting. The synthesized In$_2$O$_3$ cubes possess superior PEC activity and excellent chemical and structural stability in OER on account of the unique surface structure and electronic band structure of the {001} facets. Our results reveal that it is feasible to promote the PEC water splitting efficiency of photoanode materials by controlling the growth on specific crystal facets. The technique and concept can be extended to other facet-specific materials in applications such as sensors, solar cells, and lithium batteries.

## ASSOCIATED CONTENT

### Supporting Information

Experimental methods, SEM images, TEM and SAED, XRD patterns, and UV/vis absorption spectra of In$_2$O$_3$ microcrystals with various morphologies, schematic of three-electrode electrochemical cell and experimental apparatus, pressure curves as a function of temperature for In$_2$O$_3$ crystal, and stability measurement for continuous 20 h. This material is available free of charge via the Internet at http://pubs.acs.org.
REFERENCES


Supporting Information

Cubic In$_2$O$_3$ Microparticles for Efficient Photoelectrochemical Oxygen Evolution

Ming Meng$^1$, Xinglong Wu$^{1,2,*}$, Xiaobin Zhu$^1$, Lun Yang$^1$, Zhixing Gan$^1$, Xiaoshu Zhu$^3$, Lizhe Liu$^1$, and Paul K. Chu$^4$

$^1$ Key Laboratory of Modern Acoustics, MOE, Institute of Acoustics, Collaborative Innovation Center of Advanced Microstructures and Department of Physics, Nanjing University, Nanjing, 210093 P. R. China

$^2$ Department of Physics, NingBo University, NingBo 3153001, China

$^3$ Center for Analysis and Testing, Nanjing Normal University, Nanjing, 210093 P. R. China

$^4$ Department of Physics and Materials Science, City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong, China

Corresponding Author

*E-mail: hkxlwu@nju.edu.cn (X.L.Wu)
Experimental methods

Sample preparation: The indium oxide (In$_2$O$_3$) microcrystals were prepared at ambient pressure using an improved CVD system as illustrated in Figure S1 in Supporting Information. An n-Si (100) wafer (1-10 Ω·cm resistivity, 0.5 mm thick, and 1×1 cm$^2$) covered by a 10 nm gold thin film served as the substrate for the fabrication of In$_2$O$_3$ microcrystals and was placed downstream in a small quartz tube (inner diameter of 1.6 cm and length of 20 cm) which was positioned in the center of a big horizontal quartz tube (inner diameter of 5.2 cm and length of 120 cm) in a furnace. Mixed powders of In$_2$O$_3$ (0.35 g) and active carbon (0.15 g) as source materials were put on an alumina boat adjacent to the Si substrate as shown in Figure S1. During the fabrication of In$_2$O$_3$ microcrystals, the furnace was respectively heated to 920, 940, 960, 980, and 1000 °C at a heating rate of 50 °C and remained at the respective temperature for 3 h under a mixture of Ar (98%) and O$_2$ (2%) at a constant flow rate of 150 sccm (standard cubic centimeter per minute). To determine the relationship between supersaturation (growth temperature) and relative growth rate of the crystal facets, we pay our attention to the growth process of In$_2$O$_3$ microcrystals at 1000 °C. Time-dependent morphology evolution experiments were carried out by intercepting intermediate products in different reaction stages at 10, 20, 30, 60 and 90 min. The film thicknesses of the five samples with different morphologies were measured using a Zeta 20 (Zeta Instruments, United States) and the samples were found to have the same thickness of 22.7 μm.
**Characterization:** The morphology and crystallography of the samples were determined on FE-SEM (Hitachi S4800), high-resolution transmission electron microscopy (HR-TEM, JEOL-2100), and X-ray powder diffraction (XRD, Philips, Xpert). The diffuse reflectance spectra were recorded on a VARIAN Cary5000 spectrophotometer. A series of photoelectrochemical tests was conducted using a deaerated (purified with N₂) three-electrode configuration connected to a CHI 660D work station (CH Instrument) at about 25 °C employing an epoxy-sealed In₂O₃ microcrystals sample with an exposed area of 0.8 cm² as the working electrode, Pt mesh as the counter electrode, Ag/AgCl (3 mol L⁻¹ KCl-filled) as a reference electrode, and 1 M NaOH (pH, 13.6) as the electrolyte (see Figure S12 in Supporting Information). On the backside of the Si substrate, an ohmic contact was established using eutectic gallium-indium alloy. White light was supplied by a 500 W Xe lamp and a water filter was applied to reduce infrared heating of the electrolyte. The illumination power on the sample was adjusted from 270, 240, 160 to 100 mW/cm² by changing the Xe lamp power from 500 to 200 W, and measured by a Si photodiode. The impedance data were collected under an AC perturbation signal of 5 mV over the frequency range between 10,000 and 0.01 Hz. In the chemical and structural stability tests, the amperometric I–t data were acquired at 0.22 V vs. Ag/AgCl. The thermodynamic potential for oxygen evolution was determined by Nernst equation: 

\[
E_o (O_2/H_2O) = 1.23 - 0.05917 \text{pH} = 0.42 \text{V}_\text{NHE} = 0.22 \text{V}_\text{AgCl/Ag}.
\]

**Oxygen measurement:** An Ocean Optics oxygen sensor system equipped with a FOXY probe (NeoFox Phase Measurement System) was used to quantify oxygen.
evolution. The experiment was carried out together with the chemical and structural stability tests (see Figure S12 in Supporting Information). Prior to the O₂ measurement, the headspace of the anodic compartment was degassed by high purity N₂ (99.9995%) for 1 h under vigorous stirring. PEC water splitting with O₂ sensing was continued for 150 min at 0.22 V vs. Ag/AgCl and the O₂ yield was used to calculate the Faradic efficiency.
Figure S1. Schematic illustration of the tube-in-tube system for the preparation of In$_2$O$_3$ microcrystals with different morphologies. The main advantage of this CVD system is to use a small-diameter quartz tube to increase the supersaturation of the reagent species and thus size-uniform In$_2$O$_3$ particles with various morphologies can be produced with large area and high yield.
Figure S2. Low-magnification (x1300) FE-SEM image of the as-fabricated In$_2$O$_3$ cubes revealing abundant cubes on the silicon substrate.
Figure S3. XRD patterns collected from In$_2$O$_3$ microcubes and blank Si substrate.
Figure S4. Panoramic views of the as-synthesized In$_2$O$_3$ microcrystal polyhedrons with various morphologies: (a,b) truncated cubes, (c,d) cuboctahedrons, (e,f) truncated octahedrons, and (g,h) octahedrons.
**Figure S5.** XRD patterns collected from different In$_2$O$_3$ microcrystals. A standard XRD pattern of In$_2$O$_3$ is also provided. The intensity ratio of the (400) to (111) peaks diminishes from 6.5, 4.5, and 3.8 as the microcrystal morphology evolves into cubes, truncated cubes, and finally cuboctahedrons. The peaks with labels (▼) are from the Si substrate.
Figure S6. (a,b) Schematic illustration and low-magnification TEM image of a truncated cube viewed along the [001] direction. (c) Corresponding SAED pattern along the [001] direction. (e,f) Schematic illustration and low-magnification TEM image of a cuboctahedron viewed along the [111] direction. (g) Corresponding SAED pattern along the [111] direction.

Figure S6a-c display the schematic illustration, low-magnification FE-TEM image, and corresponding SAED pattern of the truncated cube along the [001] direction. The contrast difference in the four apex angles of the square projection reflects thickness variation resulting from truncation along the [111] direction. Cuboctahedron is bound by six square {001} and eight triangular {111} facets, and the joints among the facets are the edge of [110]. The projection is hexagonal along the [111] direction as shown in Figure S6e-f. The tetragonal (Figure S6c) and hexagonal symmetric (Figure S6g) SAED patterns reveal that both the truncated cube and cuboctahedron are bound by six {001} and eight {111} facets and the ratios of the surface areas of these facets are different.
Figure S7. UV/Vis absorption spectra of In$_2$O$_3$ cubes, truncated cubes, and cuboctahedrons. The inset shows the curve of the transformed Kubelka-Munk function vs. incident light energy of the In$_2$O$_3$ cubes.
Figure S8. Pressure curves as a function of temperature for In$_2$O$_3$ crystal.

The carbothermal reduction in the In$_2$O$_3$ microcrystal growth includes two steps:

\[
\text{In}_2\text{O}_3(S) + 2C(S) \rightarrow \text{In}_2\text{O}(V) + 2\text{CO}(V)
\]  
(1)

\[
\text{In}_2\text{O}(V) + \text{O}_2 \rightarrow \text{In}_2\text{O}_3(V)
\]  
(2)

\[
2\text{CO} + \text{O}_2 \rightarrow 2\text{CO}_2 .
\]  
(3)

Firstly, reduction of the In$_2$O$_3$ powder by active carbon produces In$_2$O vapor and CO at a high temperature according to reaction (1). Secondly, In$_2$O is oxidized according to reaction (2) forming In$_2$O$_3$ that is transported to the substrate with the aid of the carrier gas. Here we mention that CO gets easily oxidized to form CO$_2$ when it reacts with O$_2$ at high temperature according to reaction (3). However, the influence of CO oxidation on the evolution of In$_2$O to In$_2$O$_3$ is negligible because the gas flow rate of 150 sccm (Ar: 98% and O$_2$: 2%) in the reaction chamber with a small-diameter growth tube is high enough to complement the loss of oxygen gas. The vapor pressure of In$_2$O is calculated by the following relation:

\[
\log P_{\text{In}_2\text{O}} = \left( - \frac{41650}{T} \right) + 15.438 .
\]  
(4)

Because the reaction occurs in an oxygen atmosphere, the vapor pressure of In$_2$O$_3$ is
proportional to that of In$_2$O. Accordingly, it may be inferred that the vapor pressure of In$_2$O$_3$ is determined by the temperature. The temperature-dependent pressure profile is shown in Figure S8 and the vapor pressure of In$_2$O$_3$ increases with temperature.
Figure S9. Simulated and magnified SEM images of In$_2$O$_3$ particles prepared at 1000 °C for different periods of times: (a) 10, (b) 20, (c) 30 min.

We have carefully examined these samples mentioned in Figures 4a-4c by employing FE-SEM observations. After the initial reaction time of 10 min, large quantity of In$_2$O$_3$ nanoparticles with hexapod-like morphology were formed over the substrate due to the faster growth rate along the <001> direction (Figures 4a and Figure S9a). As the growth process proceeds, the open spaces between the pods are gradually filled due to continuous growth of <111> direction (Figures 4b and S9b), and in this way, the hexapod-like particles gradually disappear and more truncated-octahedron-like nanoparticles generate and aggregate together (Figure 4c and Figure S9c). Owing to the short reaction time of 30 min and unstable growth conditions during the cooling process, In$_2$O$_3$ particles are easy to form different morphologies as displayed in Figure S9a-c.
**Figure S10.** Simulated and magnified SEM images of In$_2$O$_3$ particles prepared at 1000 °C for different periods of time: (a-b) 60 min; (c-d) TEM image and SAED pattern (inset in (d)) of the intermediate In$_2$O$_3$ microcube along [001] direction and slightly tilted; (e-f) 90 min.
Figure S11. SEM images of In$_2$O$_3$ particles prepared at 1000 °C for different gas flow rate: (a) 150 sccm; (b) 100 sccm.
**Figure S12.** Three-electrode electrochemical cell configuration. A series of photoelectrochemical tests are conducted in a deaerated (purified with N₂) three-electrode configuration connected to a CHI 660D work station (CH Instrument) at ~25 °C employing an epoxy-sealed In₂O₃ microcrystal sample with an exposed area of 0.8 cm² as the working electrode, Pt mesh as the counter electrode, Ag/AgCl (3 mol L⁻¹ KCl-filled) as a reference electrode, and 1 M NaOH (pH, 13.6) as the electrolyte. On the backside of the Si substrate, an ohmic contact is formed with eutectic gallium-indium alloy. White light is provided by a 500 W Xe lamp and a water filter is placed between the lamp and electrochemical cell to reduce the infrared heating effect on the electrolyte. The working compartment is fitted with a FOXY OR 125-73 mm O₂ sensing probe connected to a Multi-Frequency Phase Fluoro-meter.
Figure S13. Current versus voltage (J-V) curves of the In$_2$O$_3$ polyhedral photoanodes. The curves are obtained from a 1 M aqueous NaOH (pH = 13.6) solution under illumination (270 mW/cm$^2$).
Figure S14. (a) Current versus voltage (J-V) curves of the microscale In$_2$O$_3$ cube photoanodes under 500 W xenon lamp illumination with different low-pass optical filters in a 1 M aqueous NaOH (pH = 13.6) solution. (b) Plot of the photocurrent...
Figure S17. (a) Low-magnification FE-SEM image and (b) XRD pattern of the In$_2$O$_3$ cubes after undergoing the PEC water splitting reaction for 150 min. The In$_2$O$_3$ cubes show no obvious change in the surface morphology and crystal phase afterwards.
densities at a potential of 0.22 V vs. Ag/AgCl under irradiation by the labeled wavelength range. (c) Current versus voltage (J-V) from the In$_2$O$_3$ cubes/Si substrate displaying low resistivity between the Si and In$_2$O$_3$ junction.

The wavelength-dependent photoelectrocatalytic tests are performed using various low-pass optical filters to determine whether the Si substrate participates in the photocurrent. Under irradiation by UV-blue light, the In$_2$O$_3$ cubes/Si substrate shows a large photocurrent response, but the response is reduced largely when irradiated by 500-700 nm light (Figure S14a-b). Since the photoexcited electron-hole pairs can still be produced under 500-700 nm irradiation for the Si substrate, the enhanced photocurrent response is not due to the Si substrate. In addition, the charge transport across the Si substrate/In$_2$O$_3$ junction is examined based on the J-V characteristics and a similar conclusion is obtained (Figure S14c).
Figure S15 Nyquist plots measured under illumination of the In$_2$O$_3$ octahedron, cubotahedron and cube photoanode at an applied potential of 0.22 V vs. Ag/AgCl.

Under illumination, two semicircles are clearly observed from the In$_2$O$_3$ octahedrons, cubotahedrons and cubes. The low-frequency semicircle associated with trapping of holes is clearly much smaller for In$_2$O$_3$ cubes in comparison with cuboctahedrons and octahedrons. The results clearly show that the In$_2$O$_3$ cubes possess a much smaller hole transfer resistance from the surface than octahedrons, thus suggesting the existence of a surface state (a valance sub-band) on the In$_2$O$_3$ {001} facet where holes gather.
Figure S16. (a) Stability measurement of a typical In$_2$O$_3$ microcube photoanode performed at 0.22 V$_{\text{Ag/AgCl}}$ in a 1 M aqueous NaOH (pH = 13.6) solution under illumination (270 mW/cm$^2$). (b) Amount of O$_2$ gas leaked from the test device in the absence of the In$_2$O$_3$ cube photoanode.

It can be seen that the photocurrent is stable at 2.1 mA/cm$^2$ for 20 h under continuous illumination (Figure S15a). In addition, the amount of O$_2$ gas leaked from the test device is 2.47 µmol and accounts for 5% in the given 150 min test (Figure S14b in Supporting Information). Hence, the 8% loss in the Faraday efficiency in 150 min may be due to gas leakage.