Turning Indium Oxide into a Superior Electrocatalyst: Deterministic Heteroatoms

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The efficient electrocatalysts for many heterogeneous catalytic processes in energy conversion and storage systems must possess necessary surface active sites. Here we identify, from X-ray photoelectron spectroscopy and density functional theory calculations, that controlling charge density redistribution via the atomic-scale incorporation of heteroatoms is paramount to import surface active sites. We engineer the deterministic nitrogen atoms inserting the bulk material to preferentially expose active sites to turn the inactive material into a sufficient electrocatalyst. The excellent electrocatalytic activity of N-In₂O₃ nanocrystals leads to higher performance of dye-sensitized solar cells (DSCs) than the DSCs fabricated with Pt. The successful strategy provides the rational design of transforming abundant materials into high-efficient electrocatalysts. More importantly, the exciting discovery of turning the commonly used transparent conductive oxide (TCO) in DSCs into counter electrode material means that except for decreasing the cost, the device structure and processing techniques of DSCs can be simplified in future.

Increasing energy demands have stimulated intense research on electrocatalysts for oxygen reduction reaction, water reduction reaction and triiodide (I⁻⁻) reduction reaction etc, which are at the heart of the typical key renewable-energy technologies such as fuel cells¹–², water splitting³–⁴, dye-sensitized solar cells (DSCs)⁵–⁶ and so on. Platinum (Pt) is always the suitable electrocatalyst for these reduction reactions due to its high conductivity, good catalytic activity and chemical stability, but its low abundance ratio and high costs precluded the large-scale utilizations of these new energy technologies. These considerations have led to ongoing efforts to design molecular catalysts that employ earth-abundant materials, to match up to or surpass the catalytic activity of Pt. Because high electric conductivity and good catalytic activity are the two main requirements for an efficient electrocatalyst, screening the alternatives among the abundant conductive materials like conductive oxides is a reasonable way. However, according to our previous theoretical research⁷, some conductive oxides such as indium oxide (In₂O₃), stannic oxide (SnO₂) and zinc oxide (ZnO) are unfortunately proven to be electrocatalytically inactive, due to their low adsorption energies of reactant molecules and scarce active sites which are necessary for adsorption of the reactants, bond-breaking and bond-formation, and desorption of the products in the heterogeneous catalytic process⁸. To deliver these intrinsically inactive but abundant materials into active catalysts, one needs to control the atomic-scale surface structure to preferentially expose a greater fraction of the active sites⁹ or exhibit a higher adsorption energy, which is highly challenging but desirable.

Along the way, recent studies have shown that doping the carbon nanotubes and graphene with heteroatoms or defects sites can introduce electrocatalytic active sites for oxygen reduction in fuel cells¹⁰,¹¹ and for I⁻⁻ reduction in DSCs¹²,¹³. Similarly, nitrogen-doped indium oxide (N-In₂O₃) can be photocatalytically active for water splitting¹⁴–¹⁶. More remarkably, the nitrate-type species in interstitial sites have been identified as an important role in the photovoltaic improvement of N-In₂O₃¹⁴. However, such design strategies have rarely been based on molecular-level understanding of the reaction mechanism. In addition, how the heteroatoms transform the metal oxide with scarce active sites into high-efficiency catalysts with sufficient active sites has been unexplored. Within the density functional theory (DFT) framework, the adsorption energy of I atom (E(ad)) on the common (110)
surface of In$_2$O$_3$ is found to be increased significantly when the interstitial N atoms are imported, which predicts that interstitial N-In$_2$O$_3$ could be catalytically active.

Herein, directed by this prediction, we describe our efforts to turn abundant In$_2$O$_3$ into a superior electrocatalyst by atomic-scale doping. We accomplish this through a facile one-step solution strategy to introduce trace amount of interstitial N atoms to In$_2$O$_3$ nanocrystals via decomposition of indium nitrate, which serves as both reagent and dopant source. To the best of our knowledge, this is the first report of interstitial N-In$_2$O$_3$ nanocrystals synthesized by a wet chemical technique. Further, the resultant N-In$_2$O$_3$ nanocrystals supported by fluorine-doped tin oxide (FTO) glass substrates were applied as counter electrode (CE) in DSCs for the first time. Amazingly, the DSCs with N-In$_2$O$_3$ CE achieved a power conversion efficiency ($\eta$) of 7.78% versus 7.17% for Pt under the same conditions, whereas the undoped In$_2$O$_3$ shows a $\eta$ of only 0.96%. Furthermore, in order to understand how the trace nitrogen atoms turn the inactive In$_2$O$_3$ into a superior catalyst over Pt for I$_3^-$ reduction, the catalytic activity of interstitial N-In$_2$O$_3$ towards I$_3^-$ reduction was investigated by means of DFT calculations in detail.

**Results**

To explore the effect of interstitial N-doping on the catalytic activity of In$_2$O$_3$ toward I$_3^-$ reduction reaction, we firstly performed DFT calculation to investigate the doping configuration in In$_2$O$_3$ and its adsorption toward I atom, aiming at providing a preliminary understanding for experimental synthesis. In pure In$_2$O$_3$ bulk, there exist two kinds of six-coordinated In atoms, forming a relatively regular and distorted octahedron structure, in which almost all the (at least seven kinds) possible initial structures for interstitial N-doping were optimized to identify the most stable one. The most stable configuration achieved is shown in Figure 1a. One can see that the inserted N atom prefers to bond with two lattice O atoms and an In atom, forming a local NO$_2^-$ configuration with a bond length of N-O of $\sim$1.36 Å, in which the two oxygen atoms deviate evidently from their original lattice site in In$_2$O$_3$ and the number of O-In bond is reduced from 4 to 2. Bader charge analysis indicates that these two O atoms are charged with $\sim$ -0.77 e that is evidently less than the other O atoms ($\sim$ -1.26 e), and N exhibits an oxidized state (denoted as N$^{2-}$ with $\delta$ = 0.14 e). Based on this stable configuration, In$_2$O$_3$(110), one of the most exposed surfaces of In$_2$O$_3$, was modelled with interstitial N dopant at the near-surface (see Figure 1b and c). It shows that the doped N atom tends to be located at the subsurface and bind with the surface five-coordinated In atom at a distance of 2.30 Å, thus it can be expected that the binding ability of this kind of surface In atom toward I or I$_2$ could be tuned due to the change of coordination environment. We calculated the adsorption of I atom at this five-coordinated surface In atom at the gas/solid interface, and the adsorption energy (relative to half an I$_2$ molecule) was calculated to be $-0.54$ eV for N doped In$_2$O$_3$(110), which is much enhanced compared to that (0.45 eV) of the pure In$_2$O$_3$(110) (see Figure 1b).

The adsorption of I atom at the interfaces of CH$_3$CN/In$_2$O$_3$(110) with or without N doping was also calculated, which increase to $-0.94$ and 0.16 eV, respectively, but give the same trend. Based on the thermodynamics model verified previously$^{13,14}$, demonstrating that the $E_{ad}^*$ at the CH$_3$CN/electrode interface can serve as a descriptor for the iodine reduction activity, and it should usually range from around $-0.33$ to $-1.20$ eV for good catalysts. Thermodynamically, when $E_{ad}^*$ is evidently weak, the dissociation of I$_2$ molecule would hardly proceed; while $E_{ad}^*$ is too strong, the overall activity can be limited by I$^-$ removal into I$^-$ (sol) owing to the large energy requirement. It is clear that the adsorption energy of I atom on In$_2$O$_3$ resulting from the interstitial N doping is well within required thermodynamic range for a good catalyst to catalyze triiodide reduction, suggesting the potentially enhanced catalytic activity of N-In$_2$O$_3$.

Directed by the theoretical estimation, N-In$_2$O$_3$ nanocrystals were synthesized by a smart and facile one-pot solution process (see the Methods). The scanning electron microscopic energy-dispersive x-ray (SEM-EDX) analysis in Figure S1 (shown in SI) indicates that trace amount of N atoms of about 5.46 at.% were doped. In order to examine chemical changes caused by the doping with N atoms and the doping position of N atoms in In$_2$O$_3$, nanocrystals, the X-ray photoelectron spectroscopic (XPS) measurements were carried out. The XPS spectra of N-In$_2$O$_3$ sample recorded is shown in Figure 2a–b for N 1s and O 1s core levels, and the survey spectrum and high-resolution In 3d XPS are shown in Figure S2–S3. Nitrogen 1s core level shows a single peak at 399.3 eV, which appears at higher binding energy (BEs) than the typical energy for InN (397 eV$^{16}$, or 396.5 eV$^{17}$) and at lower BEs than free or adsorbed N species on metal oxides. According to the literature about N-doped In$_2$O$_3$$^{15,14,16}$ or N-doped TiO$_2$$^{19}$, nitrogen atoms substitutionally doped into the In$_2$O$_3$ lattice (In-N-In linkages) own the characteristic peak at approximate 397 eV, which does not appear in the XPS of our sample, and on the contrary, the peak at 399.3 eV in our sample can be attributed to a characteristic peak of interstitial N, being NO$_2^-$ located in an interstitial position. The N-In$_2$O$_3$ sample shows a single peak at 444.0 eV for In 3d 5/2, which is attributed to In$_2$O$_3$ according to the NIST XPS database (444.30 to 446.7 eV). This small lower BE shift may be due to an interstitial doping$^{20}$. Gaussian fitting of the O 1s region shows two peaks at 529.4 and 531.0 eV. The former peak can be attributed to the In-O bond in In$_2$O$_3$$^{11,13,15}$, and the peak at 531.0 eV is the characteristic of a non-stoichiometric oxide, oxynitride, or adsorbed water$^{19,21}$. It is worth noting that the peak at 531.0 eV overwhelms the peak at 529.4 eV of pristine In$_2$O$_3$. This result indicates that the interstitial N enables the sample adsorb the foreign hydroxyls more easily$^{18}$, which is consistent with our theory prediction of the increasing $E_{ad}^*$ at the acetonitrile/electrode interface. The morphology and crystallinity of as-prepared N-In$_2$O$_3$ nanocrystals were analyzed using transmission electron microscopy (TEM) and high-resolution TEM (HRTEM). Figure 2c shows the TEM image of quasi-monodisperse N-In$_2$O$_3$ nanocrystals and the nanocrystal diameter.

**Figure 1** Structures of interstitial N doping and I atom adsorption. (a) The most stable bulk structure of interstitial N-doped In$_2$O$_3$ (N-In$_2$O$_3$); (b) top view of the optimized surface structure of N-In$_2$O$_3$(110); (c) side view of the optimized I adsorption structure on N-In$_2$O$_3$(110). Red, brown, blue and purple balls represent O, In, N and I, respectively. Marked in circle shows the local configuration of NO$_2^-$ resulting from the interstitial N doping, and dark brown balls indicate the distorted lattice O accompanying the N doping.
was approximately \((9 \pm 2)\) nm. From Figure 2d, it can be seen that the N-In\(_2\)O\(_3\) nanocrystal is mainly bounded by \{440\} facets. As shown in Figure S4 in SI, all X-ray diffraction (XRD) peaks of the synthesized N-In\(_2\)O\(_3\) can be indexed to the lattice planes of body-centered cubic In\(_2\)O\(_3\) (JPCDs no. 71-2194), which is consistent with the TEM result. It is worth noting that compared to conventional costly preparation of irregular N-In\(_2\)O\(_3\) powders via high-temperature calcinating, the way to produce N-In\(_2\)O\(_3\) nanocrystals with small grain size and faceted morphology via a solution-base approach would lower the manufacturing cost and increase the catalytic activity of the material.

The performances of N-In\(_2\)O\(_3\) on I\(_3\)\(^-\) reduction and further on photovoltaic conversion efficiency of DSCs were characterized in the following parts. For comparison, platinum and undoped In\(_2\)O\(_3\) nanoctahedron synthesized according to the literature (see SI in details, SEM shown in Figure S5)\(^{20}\), were also used as CEs in DSCs constructed under the same condition in control experiments. Figure 3a shows the photocurrent-voltage (J-V) curves of three DSCs fabricated with N-In\(_2\)O\(_3\), Pt and undoped In\(_2\)O\(_3\) nanoctahedron electrodes as CEs. The detailed photovoltaic parameters from the J-V curves are summarized in Table 1. As shown in Table 1, the device equipped with N-In\(_2\)O\(_3\) yields a remarkable \(g_{\text{sc}}\) of 7.78%, which is superior to that of the device with a Pt CE, far better than that of undoped In\(_2\)O\(_3\) nanoctahedron and \(J_{\text{sc}}\) increased in the same order. These interesting results demonstrate that the interstitial N atoms surely turn In\(_2\)O\(_3\) into a superior catalyst surpassing Pt for I\(_3\)\(^-\) reduction, which is in accordance with our prediction results. To better understand the improved DSC performance for N-In\(_2\)O\(_3\) CE, electrochemical impedance spectra (EIS) experiments of the symmetrical cells fabricated with two identical N-In\(_2\)O\(_3\) and Pt CEs were carried out at 20°C, and the results are shown in Figure 3b, while the EIS of undoped In\(_2\)O\(_3\) nanoctahedron was given in SI (Figure S6). The EIS parameters were determined by fitting the impedance spectra using the ZSimpWin software via the circuit model inserted in Figure 3b, and were summarized in Table 1. The high-frequency intercept on the real axis represents the series resistance \(R_s\), which is mainly composed of the bulk resistance of CEs materials, resistance of FTO glass substrate, and contact resistance, etc. It can be seen that \(R_s\) of N-In\(_2\)O\(_3\) (7.03 \(\Omega\)) is smaller than that of Pt (9.64 \(\Omega\)), which should be benefit to the increase of the \(J_{\text{sc}}\) of N-In\(_2\)O\(_3\). While the lower \(R_s\) of N-In\(_2\)O\(_3\) than that of undoped In\(_2\)O\(_3\) (9.52 \(\Omega\)) indicates that the introduction of the interstitial N atoms increases the electric conductivity of In\(_2\)O\(_3\). The low-frequency region (the right semicircle) reflects the diffusion in the electrolyte, which is not closely related to catalysis and hence is not the focus of attention in this paper. The semicircle in the high frequency region (the left one) arises from the parallel connection of coupling between the constant phase angle element (CPE) at the CE/electrolyte interface and the charge-transfer resistance \(R_{\text{ct}}\) of CE, which is directly proportional to the diameter of the left semicircle. \(R_{\text{ct}}\) is a measure of the ease of
electron exchange between the electrode and the electrolyte and thus varies inversely with the I$_3^-$ reduction activity of the CE$s$\textsuperscript{21}. As shown in Table 1, the $R_{ct}$ of N-In$_2$O$_3$ is 5.51 $\Omega$, significantly smaller than that of Pt (8.65 $\Omega$) and much smaller than that of undoped In$_2$O$_3$ nanoctahedron (379.4 $\Omega$), which means that the N-In$_2$O$_3$ has a higher catalytic activity for I$_3^-$ reduction than that of Pt. While the so high $R_{ct}$ of undoped In$_2$O$_3$ nanoctahedron indicates that it nearly has no catalytic activity for I$_3^-$ reduction. It also can be seen that the $CPE$ of N-In$_2$O$_3$ is lower than that of Pt, which means that N-In$_2$O$_3$ has a smaller active surface area\textsuperscript{22-24}. But, it can be obtained that the low $R_{ct}$ and high catalytic activity ($R_{ct}$) of N-In$_2$O$_3$ make up its small active surface area, resulting in the high $J_{sc}$ and $\eta$ of DSCs with N-In$_2$O$_3$. In order to further elucidate the catalytic activities of different CEs, we also performed the cyclic voltammograms (CVs) of the I$_2$/$I^-$ redox couple on both the N-In$_2$O$_3$ and Pt electrodes. For the both electrodes, two pairs of oxidation and reduction peaks are well resolved, as shown in Figure S7. The left and right pairs are described by equations (1) and (2), respectively.

$$I_3^- + 2e^- \rightarrow 3I^- \quad (1)$$

$$3I_2 + 2e^- \rightarrow 2I_3^- \quad (2)$$

Since the CE of a DSC is responsible for I$_3^-$ reduction, we only focus on the left cathodic peak corresponding to I$_3^-$ reduction. The high peak current and large peak area of the left cathodic peak reveal that N-In$_2$O$_3$ is a significant efficient electrochemical catalyst for I$_3^-$ reduction, even better than Pt electrode\textsuperscript{25,26}. To further examine the interfacial charge-transfer properties of the I$_3^-$/$I^-$ couple on the electrode surface, Tafel polarization measurements were carried out with dummy cells, similar to the one used in EIS measurements, and the results are shown in Figure S8 in SI. From the Tafel zone at middle overpotential (with a sharp slope), we can obtain the exchange current density ($J_0$), which can also be obtained from EIS parameters via equation (3).

$$J_0 = \frac{RT}{nF\rho R_{ct}} \quad (3)$$

where $R_{ct}$ is determined by EIS data, and $R$, $T$, $n$ and $F$ have their usual significance, which means that high $J_0$ means low $R_{ct}$ and high catalytic activity. The anodic and cathodic branches of the $J$-$U$ plot (Figure S8 in SI) show a largest slop for the N-In$_2$O$_3$, indicating a highest $J_0$ on this electrode in terms of the Tafel equation\textsuperscript{27-29}, which means that N-In$_2$O$_3$ has a higher catalytic activity. These experimental results consistently show that the interstitial N atoms surely turn the intrinsically inactive In$_2$O$_3$ into an efficient electrocatalyst.

Further, to elucidate the origin of high catalytic activity of N-In$_2$O$_3$ and understand the role of the interstitial N in the performance of catalyst, a molecular level investigation into I$_3^-$ reduction reaction at the CH$_3$CN/N-In$_2$O$_3$(110) interface was conducted by virtue of DFT calculations. Herein, a full reaction energetic involving thermodynamics and kinetic are considered to demonstrate the catalytic activity of N-In$_2$O$_3$ toward I$_3^-$ reduction. With respect to the I$_3^-$ reduction reaction (I$_3^-$(sol) + 2 e$^-$ $\rightarrow$ 3I$^-$(sol)) occurring on the CE, the general consensus of the reaction mechanism can be described in the reference\textsuperscript{28} (see details in SI), which shows that the I$_2$ reduction reaction (IRR) occurring at the liquid-solid interface, can determine the overall electrocatalytic activity owing the fast solution reaction (I$_3^-$(sol) $\leftrightarrow$ I$_2$(sol) + 3I$^-$(sol)). Hence we focused our studies on the two elementary reaction steps involved in I$_2$ reduction reaction at the CH$_3$CN/electrode interface, containing I$_2$(sol) + 2 e$^-$ $\rightarrow$ 2I$^-$; I$^*$ + e$^-$ $\rightarrow$ I$^-$ (sol) to explore the activity of In$_2$O$_3$ with or without N doping. It is found that on N-In$_2$O$_3$(110) surface I$^*$ molecule can readily dissociate into two I$^*$ atoms without an obvious dissociation barrier (E$_d$<$\textsuperscript{28}$), resulting in I$^*$ sitting preferably on the top of In atom at a distance ($d_{\text{In-I}}$) of $\sim$ 2.93 Å, while it is hard on pure In$_2$O$_3$(110). The adsorbed iodine atom (I$^*$) can receive one electron and then desorb into solution in form of I$^-$ with a much elongated $d_{\text{In-I}}$ of 4.20 Å at the transition state (TS) structure, being surrounded by CH$_3$CN molecules with H atoms in methyl pointing to it. The charge density differences show (Figure 4c) that the electrons accumulate at I atom in TS (Bader: 0.69 $e$) resulting from the electron depletion at the surface In atom and the surface adsorbed CH$_3$CN molecules, and there is no orbital

![Figure 3](image-url)
that the electrons of the In$_2$O$_3$ system owing to N doping would be stand the N doping effect (see details in Table S2 in SI). It shows ionic bond, and thus Bader charge analysis is conducted to under-

with the experimental

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sociate on all these three surfaces, the dissociation of I$_2$ molecule could be expected to be fast and may be in equilibrium approxi-

mately, and one can therefore speculate that N-In$_2$O$_3$ can exhibit a good catalytic activity toward IRR owing to the lower $E^\ddagger_{\text{ads}}$, even better than Pt(111). Furthermore, we estimated the equilibrium exchange current ($i_0$) of IRR using the micro-kinetic analysis to compare their activity trend. For these three surfaces, the $i_0$ of the IRR can be determined from equation (10) in SI, which quantitatively indicates the key role of the desorption barrier of I$^*$ ($E^\ddagger_{\text{des}}$); the smaller the $E^\ddagger_{\text{des}}$, the higher the catalytic activity. Accordingly, it can be concluded that their catalytic activities toward IRR follow in the order of N-In$_2$O$_3$(110) > Pt(111) > Pt(411), being consistent with the experimental $R_{\text{ct}}$ values, CV and Tafel measurements.

At this point, one question arises: why does interstitial N doping give rise to the enhancement of I$^*$ adsorption on In$_2$O$_3$(110) surface? Geometrically, the surface five-coordinated In atom on In$_2$O$_3$(110) surface strongly bonds with four surface lattice O (O$_s$) and one sub-

surface O (O$_{\text{sub}}$). After interstitial N doping at the subsurface, this surface In atom would form a relatively weak In-N bond compared to In-O bond, reflected in a longer In-N bond length (2.37 Å vs. 2.16 Å for In-O$_{\text{sub}}$ bond). On account of the bond conversation, the enhanced binding ability of the surface In atom resulting from N doping is reasonable. Electronically, as shown in Figure 4b, the In-N bond at the I$^*$ adsorption state exhibits evident characteristic of ionic bond, and thus Bader charge analysis is conducted to under-

stand the N doping effect (see details in Table S2 in SI). It shows that the electrons of the In$_2$O$_3$ system owing to N doping would be redistributed, probably rationalized by the obvious structural distor-

tion in forming a local NO$_2^-$ doping configuration. Compared with the pure In$_2$O$_3$, the total electron of all the O atoms would decrease by 1.04 e, and the two O atoms binding directly with N atom decrease most, each giving ~0.49 e; while the total electron number of all the In atoms increases by 1.14 e, and the increased electrons were delocal-

ized at all of In atoms with a little more distributing at the surface In atoms. Upon adsorption on N-In$_2$O$_3$(110), I atom can gain 0.47 e, which mainly results from the In atoms (0.28 e) and the intrstitial N dopant (0.10 e), giving rise to a relatively strong adsorption energy toward I atom (~0.54 eV). By contrast, as In$^{3+}$ in pure In$_2$O$_3$ hardly further provide electron and there are no extra electrons on them, I$^*$ can only gain few electrons (0.29 e) from the O atoms (0.28 e) upon adsorption on pure In$_2$O$_3$(110) surface, resulting in a weak ionic bond and low adsorption energy (0.45 eV). In general, the enhance-

ment of adsorption ability of In$_2$O$_3$ due to interstitial N doping could mainly be ascribed to the electron redistribution of In$_2$O$_3$, in which more extra electrons can distribute on In atom to facilitate I$^*$ adsorp-

tion, as well as the N atom itself would provide a small number of electrons in forming a local NO$_2^-$ doping configuration.

As a whole, both experimental measurements and first-principles calculations demonstrate that the performance of In$_2$O$_3$ catalyst in catalyzing I$_3^-$ reduction can be optimized by doping N atom, and the catalytic activity of N-In$_2$O$_3$ can be even better than Pt(111) owing to its increased I$^*$ adsorption energy and lower desorption barrier.

**Discussion**

In summary, for the first time, we have prepared interstitial nitrogen-
doped In$_2$O$_3$ nanocrystals via a low cost and facile one-step solution strategy, and demonstrated that the small amounts of interstitial nitrogen can transform the intrinsically inactive In$_2$O$_3$ into a high-
efficiency catalyst in DSCs, leading to a high $\eta$ of 7.78%. Beyond this application, this work demonstrates that a cheap and abundant semi-

conductor with high electric conductivity such as In$_2$O$_3$ can be turned into an active catalyst by controlled interstitial doping of N atoms via a novel nanotechnology of a simple solution-based strat-
y, and opens a new pathway to prepare effective Pt-free electro-
catalysts. More importantly, the exciting discovery of turning the commonly used TCO in DSCs into a difunctional electrode material with both transparent conductive function and catalytic activity

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**Figure 4** | Electronic structures of intermediates and energy profiles. (a) The standard Gibbs free energy profile of IRR at various systems of Pt(111), Pt(411) and N-In$_2$O$_3$(110); (b) and (c) indicate the structure of I adsorption and desorption transition state at the CH$_3$CN/N-In$_2$O$_3$(110) interface, respectively, in which 3D isosurfaces of charge density difference before and after I atomic interacting with the electrode are also illustrated (yellow indicates the electronic accumulation and light blue for electronic depletion).
means that except for decreasing the cost, the device structure and processing techniques of DSCs can be simplified in future.

**Methods**

**Synthesis of N-In$_2$O$_3$ nanocrystals.** In a typical synthesis of interstitial N-In$_2$O$_3$ nanocrystals, 0.18 g In(NO$_3$)$_3$·4H$_2$O was dissolved in the mixture of 5 mL 1 octadecene and 5 mL hexadecane (65:35). The solution was degassed for at least 2 hours and heated at 150 °C for 1 h under magnetic stirring. Then the solution temperature was raised to 280 °C in 10 min and kept for 30 min. The product was collected by centrifugation, washed with chloroform and alcohol several times.

**Materials characterization.** The morphology and structure of the samples were characterized by high-resolution transmission electron microscopy (TEM; Tecnai 30, 300 kV). XRD patterns were recorded on the dry membrane of aqueous dispersions of the N-In$_2$O$_3$ nanocrystals on a glass wafer by a Bruker D8 Advanced Diffractometer (Japan) using Cu Kα radiation (λ = 1.5406 Å) at 40 kV. Binding elements were analysed with X-ray photoelectron spectroscopy (XPS; Kratos Axis Ultra DLD) and CASAXPS software was used to analyze the XPS data. All binding energies were referenced to the C1s peak (284.8 eV) arising from surface hydrocarbons (or possible adventitious hydrocarbon). The photocurrent–voltage performance of the DSCs was referenced to the C1s peak (284.8 eV) arising from surface hydrocarbons (or possible adventitious hydrocarbon). The photocurrent–voltage performance of the DSCs was referenced to the C1s peak (284.8 eV) arising from surface hydrocarbons (or possible adventitious hydrocarbon). The photocurrent–voltage performance of the DSCs was referenced to the C1s peak (284.8 eV) arising from surface hydrocarbons (or possible adventitious hydrocarbon). The photocurrent–voltage performance of the DSCs was referenced to the C1s peak (284.8 eV) arising from surface hydrocarbons (or possible adventitious hydrocarbon).

**Theoretical calculation.** All the spin-polarized calculations were performed with Perdew-Burke-Ernzerhof (PBE) functional within the generalized gradient approximation using the VASP code. The project-averaged wave (PAW) method was used to replace the core-valence electron interaction. To model the In$_2$O$_3$(110) surface, a seven-layer (p1×1) slab (14.406×10.187 Å) corresponding to 28 In$_2$O$_3$ units cell (140 atoms) was used, in which a vacuum layer of 15 Å was applied. Because of the large size of the supercell, k-point sampling was restricted to the Γ point only. For total energy calculations, the valence electronic states were expanded in plane wave basis sets with an energy cutoff of 450 eV, and the force convergence criterion in structural is set to be 0.05 eV/Å. The transition states were expanded in plane wave basis sets with an energy cutoff of 450 eV, and the force convergence criterion in structural is set to be 0.05 eV/Å. The transition states were expanded in plane wave basis sets with an energy cutoff of 450 eV, and the force convergence criterion in structural is set to be 0.05 eV/Å. The transition states were expanded in plane wave basis sets with an energy cutoff of 450 eV, and the force convergence criterion in structural is set to be 0.05 eV/Å. The transition states were expanded in plane wave basis sets with an energy cutoff of 450 eV, and the force convergence criterion in structural is set to be 0.05 eV/Å.

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**Author contributions**

B.Z., N.N.Z., J.F.C., H.F.W. and H.G.Y. wrote the main manuscript. J.F.C., H.F.W. prepared Figure 1 and Figure 4. B.Z. and N.N.Z. prepared other figures and Table 1. Y.H., S.Y., J.W.G., X.H.Y., J.H.Z. and H.J.Z. discussed the electrochemical section, and P.H. provided several advices for theoretical calculation. All authors reviewed the manuscript.

**Additional information**

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