Supplementary Figure 1: Electron and hole distribution in a 100 nm diameter In$_{0.25}$Ga$_{0.75}$N nanowire in the presence of ~0.37 eV upward surface band bending (inset) under certain excitation conditions.
Supplementary Figure 2: Schematic illustration of the effect of non-uniform Mg doping on the near-surface band-diagram of (a) low and (b) relatively high Mg doped nitride nanowires. For low Mg doping, the near-surface region of the nanowire remains weakly n-type. With increase in Mg cell temperature (Mg flux), Mg incorporation increases in the near-surface region, resulting in a weakly p-type nanowire surface and therefore a smaller band bending.
Supplementary Figure 3: (a) Downward band bending at the surface of $p$-type (bulk) In$_{0.26}$Ga$_{0.74}$N:Mg before equilibrium with water. The downward band bending repels the photogenerated holes toward the bulk and the electrons toward the surface. (b) At equilibrium with water the downward band bending gets reduced.
Supplementary Figure 4: EDX elemental mapping images clearly demonstrating (a) Rh distribution, (b) Cr distribution, and (c) Rh/Cr$_2$O$_3$ core/shell composite nanoparticles on the nanowire nonpolar surface. Scale bar, 20 nm. (d) Room temperature $\mu$-PL spectra from bare In$_{0.26}$Ga$_{0.74}$N:Mg nanowire and from Rh nanoparticle deposited In$_{0.26}$Ga$_{0.74}$N:Mg nanowire arrays. The reduction in PL intensity confirms the suppression of charge carrier recombination by the Rh nanoparticles. (e) Overall water splitting reaction mechanism on the nanowire photocatalyst. The oxidation of water takes place on the nanowire nonpolar surfaces, as these surfaces are highly reactive for spontaneous dissociation of water$^1$. Since the nonpolar surfaces possess low energy barrier for proton diffusion$^2$, the protons produced from water oxidation process diffuse toward the active sites (Rh/Cr$_2$O$_3$ co-catalyst deposited sites) to take part in water reduction reaction to produce H$_2$. While the Rh nanoparticles enhance water reduction reaction, the Cr$_2$O$_3$ suppresses the backward reaction to form water from evolved H$_2$ and O$_2$ on Rh nanoparticles$^3$. Detailed electrochemical and in situ spectroscopic measurement reveals that the Cr$_2$O$_3$ shell is permeable to protons and H$_2$, but not to O$_2$; therefore Cr$_2$O$_3$ does not interfere with proton reduction$^4$. 
Supplementary Figure 5: Flat-band diagram of the GaN/In$_{0.20}$Ga$_{0.80}$N nanowire heterostructure, showing the conduction-band and valence-band edge positions of GaN, In$_{0.20}$Ga$_{0.80}$N, and the underlying Si substrate. The redox potentials of water are also shown by the dotted lines. It is seen that GaN and In$_{0.20}$Ga$_{0.80}$N possess sufficient overpotential for oxidation and reduction of water. The photogenerated holes in Si substrate, however, do not possess sufficient potential for water oxidation, and hence Si substrate does not take part in overall water splitting reaction. All values of potentials are in eV relative to the vacuum level.
Supplementary Figure 6: Open circuit potential (OCP) measurement on $p$-GaN/$p$-In$_{0.20}$Ga$_{0.80}$N nanowire arrays. (a) Under dark and full arc (>200 nm) illumination. (b) Under dark and visible light (>400 nm) illumination. The difference in potentials between light and dark is positive, indicating $p$-type behavior of GaN and In$_{0.20}$Ga$_{0.80}$N nanowire arrays.
Supplementary Figure 7: The solar-to-hydrogen (STH) conversion efficiency i.e. the energy conversion efficiency (ECE) under full arc illumination with AM1.5G filter vs. incident power density. As shown, the performance of the device significantly improves at high power densities. This can be attributed to light induced band flatting effect. The estimated STH conversion efficiency can reach 1.8% under concentrated full arc illumination (~26 suns). The solid line is a guide to the eye.
Supplementary Figure 8: Weight normalized evolved H₂ and O₂ from overall neutral (pH~7.0) water splitting on Rh/Cr₂O₃ core/shell nanoparticle decorated p-GaN/p-In₀.₂₀Ga₀.₈₀N nanowire arrays (0.48 mg nanowire photocatalyst) under full arc 300 W Xenon lamp illumination with AM1.5G filter. The reaction chamber was evacuated after each cycle. No sacrificial reagents were added with water. The solid lines are guides to the eye.
Supplementary Figure 9: Top view SEM image of the $p$-GaN/$p$-In$_{0.2}$Ga$_{0.8}$N nanowire arrays. Scale bar, 1 µm.
Supplementary Figure 10: Typical output spectral distribution of 300 W Xenon lamp with AM1.5 G filter onto the sample surface.
Supplementary Note 1

Impact of surface band bending on the surface electron and hole distribution

The estimation of electron and hole concentration in the In$_{0.25}$Ga$_{0.75}$N nanowire was performed by the simulation program APSYS. Specific carrier generation is introduced uniformly in the nanowire by defining a 405 nm light input to the structure, with a constant carrier generation rate of 2.5×10$^{27}$ cm$^{-3}$ s$^{-1}$. Shockley-Read-Hall (SRH) lifetime of 100 ns$^5$ and Auger recombination coefficient$^6$ of 1×10$^{33}$ cm$^6$ s$^{-1}$ are assumed in the calculation. The nanowire diameter and surface recombination velocity are considered to be 100 nm and 5×10$^4$ cm s$^{-1}$, respectively. The surface trap density$^7$ is ~1×10$^{14}$ cm$^{-2}$. A nominally undoped nanowire structure, with acceptor-like surface traps, is first simulated$^8$. The presence of ~0.37 eV upward band bending in the near surface region is assumed, which is reduced to ~0.07 eV under photo-excitation, owing to the screening effect by photogenerated carriers$^9$. The calculated electron and hole distributions across the nanowire lateral dimension are shown in Supplementary Fig. 1. It is seen that hole concentration is ~20 times higher than that of electron in the near-surface region. The carrier distribution in p-type In$_{0.25}$Ga$_{0.75}$N with the presence of a downward surface band bending has also been calculated. Electron accumulation and hole depletion in the near-surface region was clearly observed$^{10}$.

Supplementary Note 2

Estimation of nanowire surface band bending from ARXPS

Fig. 3a shows the estimated $E_{FS}$-$E_{VS}$ for different Mg doped In$_{0.26}$Ga$_{0.74}$N nanowires. For $T_{Mg}$=190 °C, the estimated $E_{FS}$-$E_{VS}$ is ~2.1 eV, which is nearly close to the $E_{FS}$-$E_{VS}$ (~2.20 eV) of
nominally non-doped In$_{0.26}$Ga$_{0.74}$N$^{11}$, indicating that the surface of In$_{0.26}$Ga$_{0.74}$N is barely doped at $T_{\text{Mg}}=190$ °C. Consequently, a large downward band bending is present in the near-surface region, resulting in a hole depletion region on the near-surface region of the nanowire$^{12}$. The drastic reduction in $E_{\text{FS}}-E_{\text{VS}}$ with further increase in $T_{\text{Mg}}$ is attributed to the enhanced Mg dopant incorporation in the near-surface region of In$_{0.26}$Ga$_{0.74}$N (Supplementary Fig. 2). Note that, the photoelectrons generated in the GaN region of the nanowires has negligible contribution to the drastic reduction in $E_{\text{FS}}-E_{\text{VS}}$ (Fig. 3a), as the near-surface Fermi-level of GaN:Mg barely changes in this doping regime ($T_{\text{Mg}}=190$-230 °C)$^{13}$. The drastic reduction in $E_{\text{FS}}-E_{\text{VS}}$ is further attributed largely to the reduction in downward band bending at the nanowire surface. Although the downward band bending caused by $p$-type doping accelerates proton reduction at the nanowire surface, it hinders the hole transport toward the nanowire-liquid interface. Therefore, by reducing the downward band bending with optimized dopant incorporation, the photocatalytic activity of the In$_{0.26}$Ga$_{0.74}$N:Mg nanowire can be significantly improved. It is important to note that the band bending also varies when the nanowires are in equilibrium with solution and under photo-excitation.

**Supplementary Note 3**

**Band bending in equilibrium with water**

Supplementary Fig. 3a shows downward band bending on the surface of $p$-type (bulk) In$_{0.26}$Ga$_{0.74}$N ($T_{\text{Mg}}=200$ °C) prior-to equilibrium with water. This downward band bending may get reduced when it comes in equilibrium with water due to interfacial charge transfer, as illustrated in Supplementary Fig. 3b. Upon photo-excitation, the remaining band bending may
flatten out owing to the screening effect by the photogenerated carriers, which lead to enhanced carrier extraction.

**Supplementary Note 4**

*Role of Rh/Cr$_2$O$_3$ core/shell co-catalyst*

Apart from the near-surface band structure, the photocatalytic activity can also be limited by the radiative and/or non-radiative recombination inside the photocatalyst$^{14}$. In order to suppress carrier recombination and therefore enhance charge carrier extraction, Rh nanoparticles were photodeposited (see Methods) on the InGaN:Mg nanowires$^{15}$. EDX elemental (Rh, Cr) mapping (Supplementary Figs. 4a, b, c) clearly demonstrates successful deposition of Rh/Cr$_2$O$_3$ core/shell co-catalyst on In$_{0.26}$Ga$_{0.74}$N:Mg nanowire surfaces. Since the Fermi level of Rh (-4.9 eV) is more negative than the electron affinity of In$_{0.26}$Ga$_{0.74}$N:Mg (-3.95 eV), the photogenerated electrons in the conduction band can easily migrate from nanowire to Rh nanoparticles. Under the same excitation condition, the measured µ-PL emission intensity of Rh/In$_{0.26}$Ga$_{0.74}$N:Mg composite is lower than that of In$_{0.26}$Ga$_{0.74}$N:Mg, confirming the fact that the photoexcited electrons are scavenged by the Rh particles, and therefore the carrier recombination is significantly suppressed (Supplementary Fig. 4d)$^{16}$. Since Rh nanoparticles can be active sites for backward reaction to form water, a Cr$_2$O$_3$ shell layer is further photodeposited on the Rh nanoparticles. The Cr$_2$O$_3$ shell layer forms a diffusion barrier which is permeable to H$^+$ and H$_2$ but not to O$_2$$^{17}$. Therefore, the Rh nanoparticles do not take part in backward reaction. Our control experiment suggests that the activity of the nanowire photocatalyst without co-catalyst is ~4-5 times lower than that of the nanowire photocatalyst with co-catalyst. Supplementary Fig. 4e further shows the overall water splitting reaction mechanism on the nonpolar In$_{0.26}$Ga$_{0.74}$N:Mg nanowire surfaces. Note that, the
presence of a thin (~2-5 nm) GaN layer at the nanowire surface (caused by In evaporation during nanowire growth) creates additional potential barrier, which may affect the transport of electrons and holes to the nanowire-water interface. However, owing to the high excitation condition (~26 suns) in our experiments, most of the photogenerated carriers can readily overcome this barrier and reach the semiconductor-liquid interface. The concentrated illumination is of particular interest for economically viable industrial production of hydrogen from photolysis as predicted by Y. Tachibana et al. J. Turner estimated a realistic limit of the concentrated light that can be used for water splitting is in the range of 10-20 suns.

Supplementary Note 5

Surface band bending-The dominant factor

While Mg dopant incorporation significantly alters the band bending, it may also lead to the formation of defects and dislocations, and therefore increases non-radiative recombination. Additionally, the ionization energy of Mg in InGaN as well as the growth temperature of InGaN is much lower than those in GaN. As a consequence, the optimum Mg doping in InGaN is achieved at lower Mg cell temperature than that in GaN nanowires. Other possible explanations for the significantly enhanced efficiency with Mg dopant incorporation include enhanced light absorption. However, the Mg doping level in the optimized sample is quite low, ~1×10^{19} cm^{-3}, which does not alter the optical absorption and charge carrier diffusion length. Moreover, it is unlikely that Mg itself serves as a catalyst, since its density is extremely low (~1×10^{19} cm^{-3}), and the maximum efficiency does not occur in samples with very high Mg concentration. From our calculations (Supplementary Fig. 1), it is seen that a small band bending can alter the surface carrier concentration by one to two orders of magnitude. The variation of carrier concentration is
on the same order as the measured enhancement in the quantum efficiency (~ a factor 30 enhancement with optimum band bending). It is therefore suggested that band bending is the primary factor that explains the observed activity.

**Supplementary Note 6**

*Effects of high Mg doping in InGaN*

At high Mg concentration, Mg acts as donor like self-compensation centers\(^{20}\). With increase in Mg concentration, nitrogen vacancy (\(V_N\)) related defects increase, which, together with the reduced growth temperature (~650 °C), leads to degradation of the structural quality\(^{20}\). These defects work as self-compensation centers in \(\text{In}_{0.26}\text{Ga}_{0.74}\text{N}\) at high-doping levels. This could explain the reduction in photocatalytic activity for \(T_{\text{Mg}} > 200 \degree \text{C}\), as shown in Fig. 3b.

**Supplementary Note 7**

*p-Type behaviour of GaN:Mg and In\(_{0.2}\)Ga\(_{0.8}\)N:Mg from open circuit potential (OCP) measurement*

The \(p\)-GaN/\(p\)-In\(_{0.20}\)Ga\(_{0.80}\)N nanowires were characterized by OCP measurement. Using three-electrode electrochemical cell configuration, the open circuit potential was performed in 1 mol L\(^{-1}\) HBr. The \(p\)-GaN/\(p\)-In\(_{0.20}\)Ga\(_{0.80}\)N nanowire arrays (on Si substrate), a Pt wire, and a double-junction Ag/AgCl were used as the photoactive working electrode, counter electrode, and reference electrode, respectively. In-Ga eutectic alloy metal was deposited on the backside of the Si substrate to serve as an Ohmic contact. OCP measurements were performed by using a 300 W Xenon lamp (Cermax, PE300BUV) as an irradiation source. The reactor chamber was made of
quartz for ample transmittance to both UV and visible light. The direction of the OCP shift, upon illumination, can determine the conductivity type of the material\textsuperscript{21}. For $p$-type material, the shift of the OCP upon illumination will be toward more positive potential with respect to Ag/AgCl\textsuperscript{22}. As shown in Supplementary Fig. 6a, under full arc illumination the difference in potentials (with respect to Ag/AgCl) between light and dark is positive, indicating $p$-type behaviour of GaN:Mg/In$_{0.20}$Ga$_{0.80}$N:Mg nanowires. In order to explore the conductivity type of In$_{0.2}$Ga$_{0.8}$N material, an optical long-pass filter (> 400 nm) was used to excite only the In$_{0.2}$Ga$_{0.8}$N segments. As shown in Supplementary Fig. 6b, the open circuit potential upon illumination shifts to more positive potential, indicating $p$-type conductivity of the In$_{0.2}$Ga$_{0.8}$N:Mg material. The OCP for $p$-GaN/$p$-In$_{0.20}$Ga$_{0.80}$N were ~0.77 and ~0.62 V vs. Ag/AgCl under full arc (>200 nm) and visible light (>400 nm), respectively. Control experiments further suggest $n$-type behaviour (negative difference between potentials under light and dark) of the conductivity in non-doped and nominally Mg doped GaN and In$_{0.20}$Ga$_{0.80}$N segments (GaN:Mg:230 °C and In$_{0.2}$Ga$_{0.8}$N:Mg:190 °C) (not shown). This is in agreement with our ARXPS analysis (Fig. 3a), wherein the $E_{FS}$-$E_{VS}$ is comparable to that of intrinsic GaN and InGaN. Because of the large background $n$-type dopants, the nominally non-doped GaN and In$_{0.2}$Ga$_{0.8}$N show $n$-type behavior\textsuperscript{23}, which is consistent with the observed behaviour from OCP measurement. With further increase in Mg concentration in GaN and InGaN (GaN:Mg:250 °C and In$_{0.2}$Ga$_{0.8}$N:Mg:195 °C), weakly $p$-type characteristics is clearly observed (not shown). This supports our ARXPS analysis that at this doping level a weakly $p$-type nanowire surface is formed (Fig. 3a).
Supplementary Note 8

Estimation of apparent quantum efficiency (AQE), absorbed photon conversion efficiency (APCE), energy conversion efficiency (ECE), and solar-to-hydrogen (STH) conversion efficiency of the double-band p-GaN/p-InGaN nanowire photocatalyst

The simplified nanowire model for the efficiency calculation:

Light propagation and absorption inside a layered structure (Fig. 4a) can generally be calculated by using a multi-layer reflectivity model. However, because of the negligible mismatch in refractive index between GaN and InGaN for the indium composition (~20-30%) used in our structure, reflection from GaN/InGaN interfaces can be ignored for both UV (average reflection~0.05%) and visible light (average reflection~0.005%). Moreover, GaN absorption spectrum largely excludes visible light whereas InGaN can absorb both UV and visible spectrum. Furthermore, a stepwise calculation for the five-layered GaN/InGaN heterostructure (Fig. 4a) shows that the GaN cap-layers (~6 nm) in between the InGaN layers absorb very small fraction of UV (<1% of total light transmitted through the nanowires). Considering all these factors, the multilayered structure (Fig. 4a) can be simplified as a two-layered structure, having a ~130 nm long p-GaN nanowire (optimally doped at $T_{\text{Mg}}=270 \, ^\circ\text{C}$) on top, followed by a lumped ~185 nm long InGaN nanowire (optimally doped at $T_{\text{Mg}}=200 \, ^\circ\text{C}$).

In order to derive the AQE for the photocatalytic overall water splitting, the number of incident photons in the wavelength range of 200-475 nm (PL peak ~475 nm as shown in Fig. 4b) was estimated from the lamp spectrum (and corresponding filter transmission spectrum), which represents the overlapped wavelength between the absorption spectrum of InGaN/GaN nanowires and the power spectrum of the lamp. The AQE and APCE were derived using the following process. The incident power on the sample can be expressed as:
\[ P_{\text{incident}}(\lambda) = \rho_{\text{incident}}(\lambda) \times A_{\text{sample}} \times \beta_{ff} \]  

where \( A_{\text{sample}} \) is the sample area (~ 3.0 cm\(^2\)) and \( \beta_{ff} \) is the nanowire fill factor. The \( \beta_{ff} \) is assumed to be unity (assuming all the incident photons are absorbed) for the calculation of AQE, and 42.3% (calculated from top view SEM image of the nanowire arrays as shown in Supplementary Fig. 9) for the estimation of APCE. \( \rho_{\text{incident}}(\lambda) \) is the incident power intensity on the sample, which was derived by measurements using a broadband detector (Thermopile Sensor, Newport-818P-100-55) and taking into account the power spectrum of the lamp (as shown in Supplementary Fig. 10) and optical filter, while mimicking the experimental configuration.

**Calculation of the AQE and APCE using AM1.5G optical filter in the UV and visible wavelength range (200–475 nm):**

In what follows, we first describe the calculation of the AQE and APCE with the use of AM1.5G optical filter. The total incident power on the sample is estimated to be 1464 mW in the wavelength range of 200–475 nm with AM1.5G filter. The number of incident photons per second, as a function of wavelength is calculated from,

\[ N_{\text{ph}}(\lambda) = \frac{P_{\text{incident}}(\lambda)}{E_{\text{ph}}(\lambda)} \]  

where \( E_{\text{ph}}(\lambda) = \frac{hc}{\lambda} \) is the photon energy for the corresponding wavelength. The total number of incident photons per second within 200–475 nm wavelength range can be calculated as follows:

\[ N_{\text{ph,inc}}(200 \text{ }– \text{ } 475) = \int_{200}^{475} \frac{P_{\text{incident}}(\lambda) \times \lambda}{hc} d\lambda \]  

The AQE is then derived from the following equation:

\[ \text{AQE} = 2 \times \frac{\text{Number of evolved } H_2 \text{ molecules per hour}}{\text{Number of incident photons per hour}} \times 100 \% \]
The amount of absorbed power depends on the optical properties of the different layers involved, namely, water, GaN and InGaN. For the simplified model of our structure, there are only three layers and hence two corresponding interfaces, which are water/GaN and GaN/InGaN interface. Considering the large refractive index mismatch between GaN and water, on average ~10% of the incident power (both UV and visible) is reflected back from the nanowires-top surface. The absorbed power can be calculated using the refractive indices and absorption coefficients of the materials (see Ref. 13 for the detailed calculation), which is estimated to be ~412.9 mW in the wavelength range of 200-475 nm with the use of an AM1.5G optical filter. The APCE of the structure is then estimated from equation (4) by replacing the number of incident photons with that of the absorbed photons, derived as:

\[
N_{ph,abs}(200 - 475) = \int_{200}^{475} \frac{P_{absorbed,GaN+InGaN}(\lambda) \times \lambda}{hc} d\lambda
\]  

(5)

The AQE and APCE, corresponding to the entire absorption spectrum (200-475 nm) for the double-band structure, which includes both UV and part of the visible photons, were derived to be ~20% and ~74.5%, respectively. The light trapping and scattering effect have not been taken into account for the estimation of APCE. Clearly, this APCE of the nanowire structure is largely limited by the charge transport efficiency to the solid-liquid interface (\(\eta_{transport}\)) and the efficiency of interfacial charge transfer (\(\eta_{interface}\)).

**Calculation of the AQE and APCE in the visible wavelength range (400-475 nm):**

From equations (3)-(5), the total incident (on the ~3 cm\(^2\) sample) and absorbed (by the nanowires) power in the visible wavelength range (400-475 nm) were calculated to be 843 mW and 153 mW, which corresponds to ~12.3% and ~68.5% AQE and APCE, respectively.
**Calculation of ECE using AM1.5G filter in UV and visible wavelength range (200-475 nm):**

The ECE was calculated to be \( \sim 7.5\% \) from the following equation\(^\text{21}\), considering the total incident power intensity in the wavelength range 200-475 nm (488 mWcm\(^{-2}\)), and \( \text{H}_2 \) evolution rate of \( \sim 1660 \mu \text{mol h}^{-1} \) (3.45 mol h\(^{-1}\) g\(^{-1}\) shown in Fig. 4d).

\[
ECE = \frac{H_2 \left( \frac{\text{mmol}}{s} \right) \times 237 \text{ kJ} \times 1000}{\rho_{\text{incident total}} \left( \frac{\text{mW}}{\text{sq.cm}} \right) \times A_{\text{sample}} (\text{sq.cm})} \times 100 \ %
\]  

(6)

Subsequently, the solar-to-hydrogen (STH) conversion efficiency (Supplementary Fig. 7) i.e. the ECE under full arc illumination with AM1.5G filter is estimated from equation (6), considering the total incident power intensity in the wavelength range 200-1100 nm.
SUPPLEMENTARY REFERENCES


