

# One-Step Overall Water Splitting under Visible Light Using Multi-Band InGaN/GaN Nanowire Heterostructures

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## S1. On the valence state of the co-catalyst particles

To confirm the presence and the valence state of the Rh/Cr<sub>2</sub>O<sub>3</sub> co-catalyst nanoparticles on the InGaN/GaN nanowires, XPS analysis was performed after photodeposition (before overall water splitting). Figure S4 shows a high resolution XPS spectrum of (a) Rh3d, and (b) Cr2p core level electrons before overall water splitting. After deconvolution using Lorentzian-Gaussian mixing functions (L/G=30%), two spin-doublets were clearly resolved from Rh3d peak. The Rh3d<sub>5/2</sub> peak observed at 307.5 eV (blue line) is attributed to metallic rhodium Rh(0).<sup>1</sup> This value is slightly higher than the reported values for bulk metallic Rh (307.2 eV), and is commonly observed in nano-sized metal particles due to initial and final-state effects.<sup>2</sup> The Rh3d<sub>5/2</sub> peak at 309.69 eV (red line) is attributed to a mixed Rh-Cr oxide, indicating the interaction between Rh and Cr nanoparticles.<sup>3</sup> The areas of the two deconvoluted XPS peaks (Figure S4a) correspond to 16.15% Rh in metallic (Rh<sup>0</sup>) form and 83.85% in mixed Rh-Cr oxide form. The deconvolution of Cr2p peak reveals one spin-doublet as shown in Figure S4b. The Cr2p<sub>3/2</sub> peak, appeared at 576.9 eV is in good agreement with the reported values for Cr<sub>2</sub>O<sub>3</sub>.<sup>3</sup> Therefore, the valence state of Cr in the co-catalyst is trivalent after photodeposition. Note that no peak was observed near 579.0 eV which is assigned to Cr<sup>6+</sup>; indicating that all the Cr<sup>6+</sup> species in the precursor (K<sub>2</sub>CrO<sub>4</sub>) is photoreduced to form Cr<sub>2</sub>O<sub>3</sub> after photodeposition. The surface compositions of Rh and Cr<sub>2</sub>O<sub>3</sub> were 2.62 and 3.36 At.%, respectively, as estimated from the areas of the corresponding XPS peaks after Shirley background subtraction. A controlled experiment further confirmed that the deposited nanoparticles were indeed caused by photodeposition, and not via other processes, such as, physical deposition without the influence of light irradiation.

## S2. On the stability of Rh/Cr<sub>2</sub>O<sub>3</sub> co-catalyst

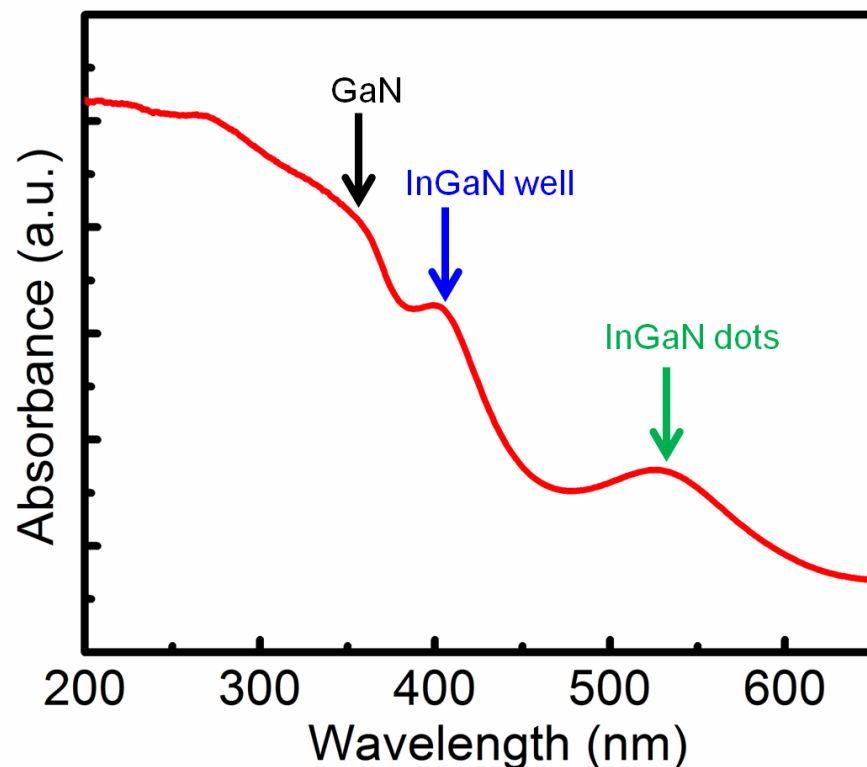
The Rh3d XPS peaks after overall water splitting reactions are shown in Figure S4. Whilst the XPS peak position remained unchanged during the course of reaction, the XPS peak area (Figure S4a) for metallic Rh (307.5 eV) decreased from 16.15% (before the reaction) to 7.4% (after the reaction); suggesting that the metallic Rh particles are oxidized during the course of reaction. This is presumably due to the fact that some of the Rh particles may not be fully covered by the Cr<sub>2</sub>O<sub>3</sub> and therefore is vulnerable to oxygen. Also, even though

the At.% of Rh3d remained nearly the same after overall water splitting, the Cr2p reduced from 3.36% (before the reaction) to 2.95% (after the reaction) (Figure S4b). The reason can probably be attributed to corrosion and hydrolysis of the Cr<sub>2</sub>O<sub>3</sub> co-catalyst. This could explain a slightly reduced activity over time (Figure 4b). Also, the Cr2p peak position did not change upon ~18 hours of reaction (Figure S4b). This result also reveals that the trivalent state of the Cr did not change after the reaction.

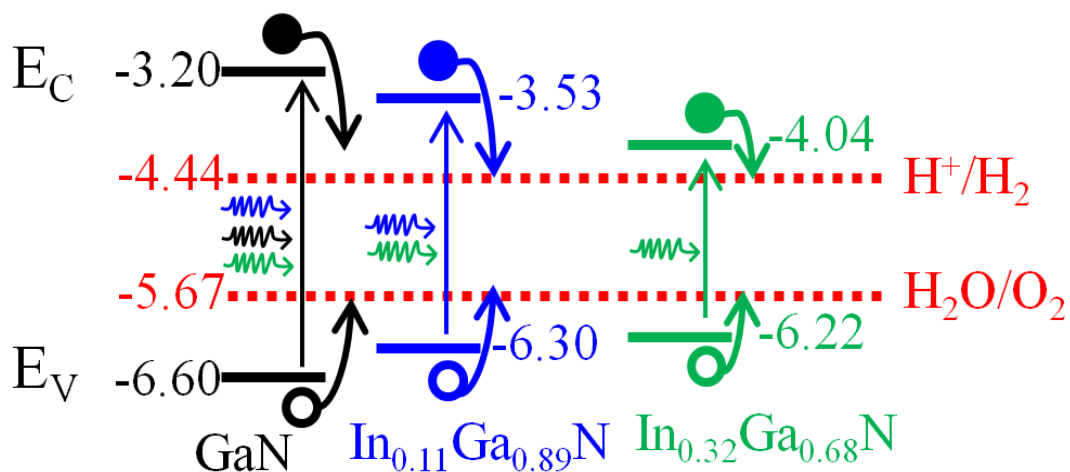
## REFERENCES

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2. Mason, M. G. *Phys. Rev. B* **27**, 748 (1983).
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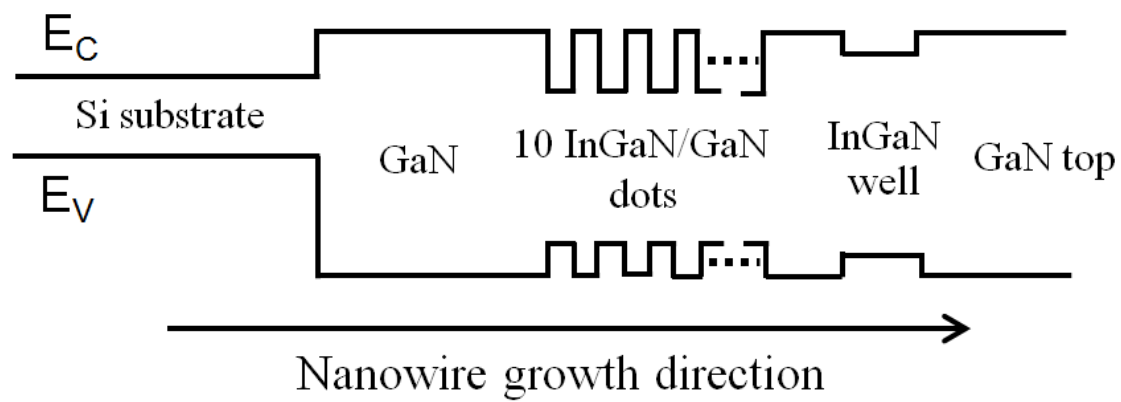
# SUPPORTING FIGURES



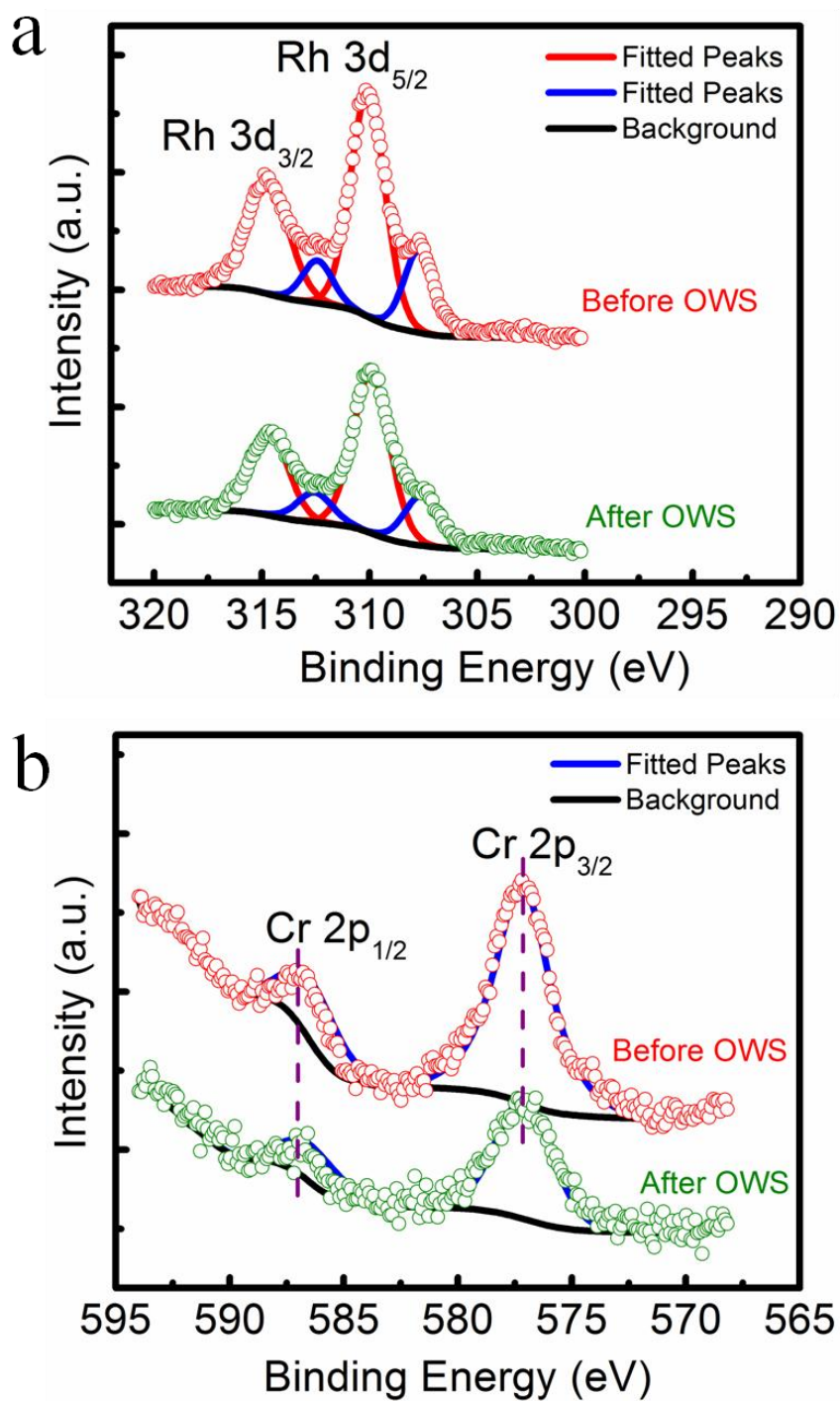
**Figure S1.** UV-Visible diffuse reflectance spectrum of InGaN/GaN nanowire heterostructure on Si substrate at room temperature.



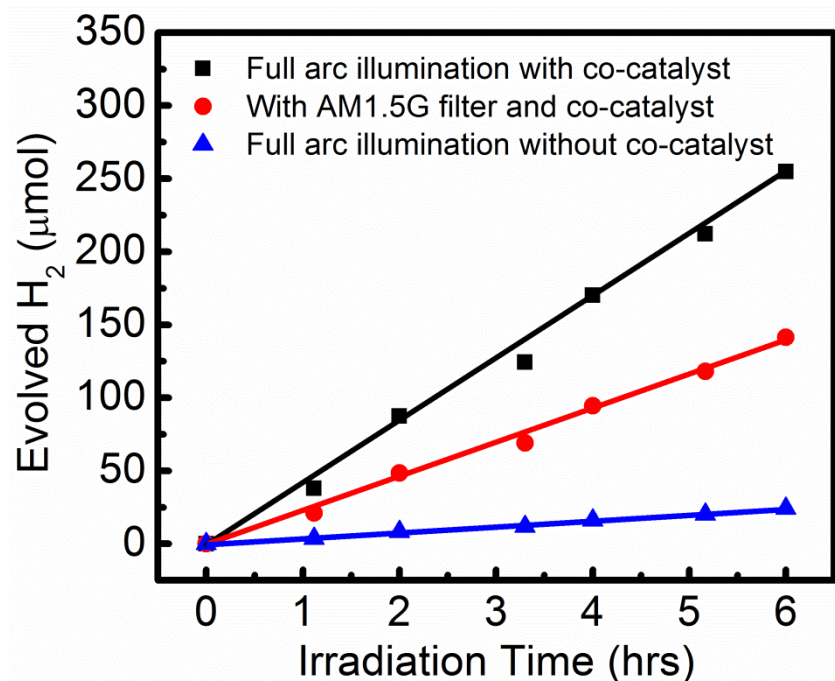
**Figure S2.** Conduction-band and valence-band edge positions of GaN,  $\text{In}_{0.11}\text{Ga}_{0.89}\text{N}$  and  $\text{In}_{0.32}\text{Ga}_{0.68}\text{N}$ , derived from Ref. 15, depict sufficient overpotential for oxidation and reduction of water. The redox potentials of water are also illustrated. All values of potentials are in eV relative to the vacuum level.



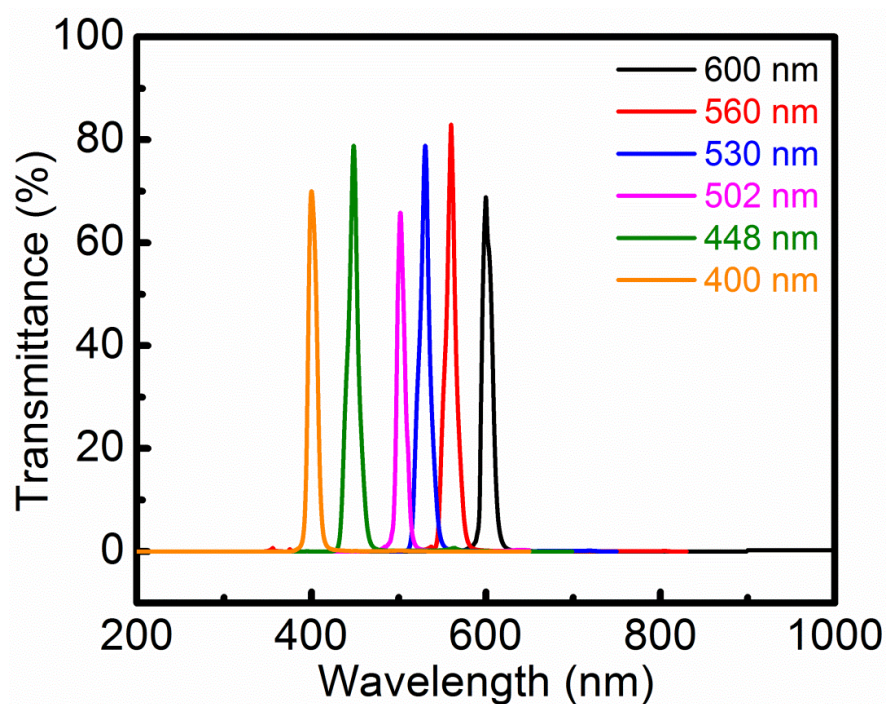
**Figure S3.** Flat band diagram of the InGaN/GaN nanowire heterostructure.



**Figure S4.** X-ray photoelectron spectroscopy (XPS) analysis of Rh/Cr<sub>2</sub>O<sub>3</sub> co-catalyst before and after overall water splitting. (a) High resolution XPS spectra of Rh3d core level electrons before and after overall water splitting (OWS). (b) High resolution XPS spectra of Cr2p core level electrons before and after OWS.



**Figure S5.** H<sub>2</sub> evolution from pure water splitting under full arc Xe-lamp, with and without Rh/Cr<sub>2</sub>O<sub>3</sub> co-catalyst deposition. For comparison, H<sub>2</sub> evolution is shown using an AM1.5G filter. The solid line is a guide to the eye.



**Figure S6.** Transmission spectra of the band-pass filters with center wavelengths from 400 to 600 nm that are used for water splitting measurements.