Electronic Supplementary Material (ESI) for Nanoscale

SUPPLEMENTARY INFORMATION

Nanowires as semi-rigid substrates for growth of thick, $In_xGa_{1-x}N$ (x>0.4) epi-layers without phase segregation for photoelectrochemical water splitting.

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EXPERIMENTAL SET UP FOR THE SYNTHESIS OF GaN NANOWIRES

Figure S1a is the schematic of the reactor used for the synthesis of GaN nanowires via thermal CVD. The reaction vessel is a double walled, water cooled stainless steel chamber. Pressure measurement is via an MKS-Baratron dual capacitance manometer and temperature is measured using a noncontact dual wavelength pyrometer. A stem runs through the bottom of the chamber via a vacuum sealed connection for the heater assembly. A serpentine tungsten filament serves as the heat source that radiatively heats a SiC (silicon carbide) coated graphite plate placed 1 cm above. The source materials (GaN powder or gallium metal) are placed on the graphite plate while the substrate (stainless steel plate) is placed 2-3 mm above the sources via graphite supports. Figure s1b is the schematic of the MOCVD reactor used for InGaN growth. The reactor has a multi precursor delivery system along with an induction heater for substrate heating. The reaction chamber is a vertical flow type with a showerhead at the top for uniform precursor distribution.

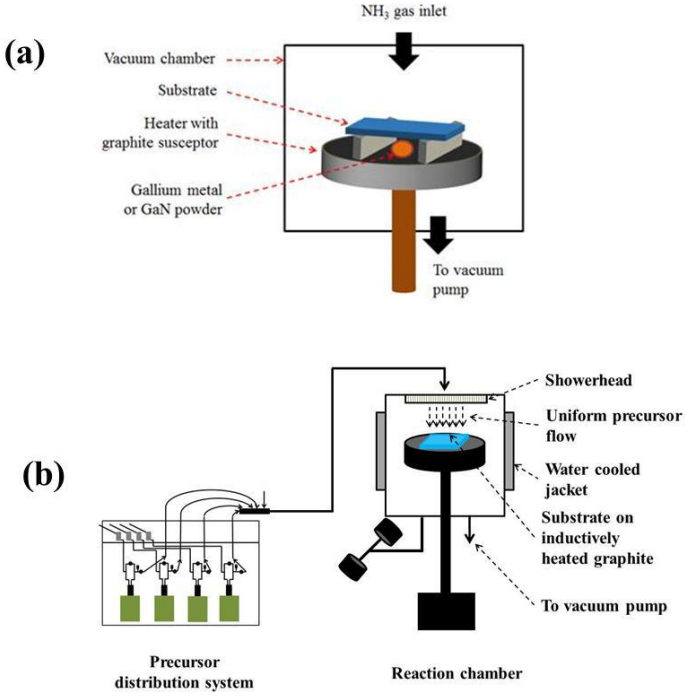


Figure S1: a) Schematic of the CVD reactor used for the synthesis of GaN nanowires. GaN powder or Ga metal was placed on the graphite susceptor and the substrate was placed 2-3 mm off the surface using graphite blocks as separators. b) Schematic of the MOCVD reactor showing the multi precursor delivery system along with the vertical flow reaction chamber with a showerhead for uniform precursor distribution and an induction heater for substrate heating.

ORENTIATION CONTROLLED SYNTHESIS OF GaN NANOWIRES

GaN nanowires were synthesized on different substrates under variations of flux and temperature conditions to investigate the influence of substrate on the growth mechanism to control the growth morphology as well as orientation. Substrates ranging from metals (copper and stainless steel), semiconductors (<100> silicon and c-GaN on sapphire) to insulators (sapphire) were employed in the study. Two different process conditions were devised to achieve different gallium flux conditions. In one case, gallium metal was heated to 750C to generate the gallium vapors in a low pressure (300 mTorr) ammonia atmosphere. In the other condition, pre synthesized GaN powder was used as the gallium source. The powder was heated to 950C in 20 Torr ammonia atmosphere.

Figure S2 shows the template to achieve the desired nanowire growth on different substrates. It is clear that substrate as well as process conditions have a big impact on the nanowire growth.

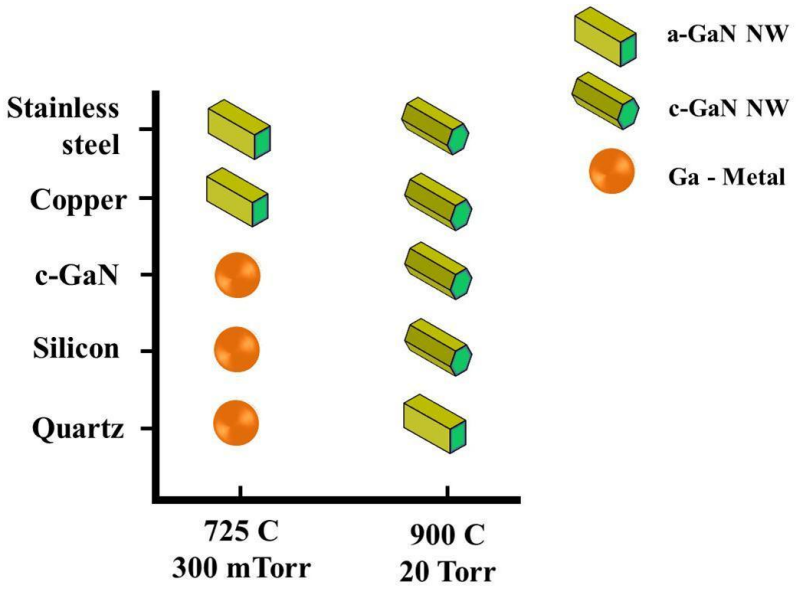


Figure S2: Template for process and substrate selection for controlled growth of GaN nanowires. Metal substrates can always be used to grow nanowires using the developed process window whereas nanowire growth on semiconductor or insulators is heavily affected by the wetting behavior of gallium.

The wetting behavior of gallium on the substrate surface controls the nuclei formation, hence the nanowire growth. Under the low temperature and high flux conditions (at 750 C using gallium metal), gallium spreads like a film on the non-metallic substrates before crystal nuclei formation can take place. However, the metals could be catalyzing the GaN formation reaction as GaN nuclei form on the metal surfaces and lead the nanowire growth. The non-metallic

substrates might are not at high enough temperatures to cause the reaction of gallium with nitrogen.

At the high temperature conditions, the surface temperature on all the substrates is high enough for the gallium flux to react and form GaN nuclei leading to nanowire growth. Here, the stability of the nuclei at the high temperatures and the interactions of the substrate control the growth orientation. C-GaN is the most stable surface at high temperatures and hence the formation of c-plane oriented nanowires on all metal and semiconductor surfaces. However, a-plane GaN nanowires grow on quartz substrates. Quartz is not a good thermal conductor and the surface might be at a lower temperature than other substrates that are good thermal conductors. At lower temperatures a-plane nuclei has lower energy of formation. This is indeed the case observed for the growth on stainless steel substrates. At higher temperatures, c-GaN nanowires are formed whereas at low temperatures, a-plane oriented GaN nanowires grow on the substrate.

COMPOSITION CONTROL OF InGaN LAYERS ON GaN NANOWIRES

As described in the article text, MOCVD was used to synthesize InGaN layers on GaN nanowires. TMGa and TMIn were used as the gallium and indium sources with NH_3 as the nitrogen source. Figure S3 is our reactor specific template/ process window for the temperature and flux based control of InGaN composition. Although it is definitely not exhaustive, this provides a good starting point to further tune the reactor and process conditions for the synthesis of InGaN layers on GaN nanowires.

R is the ratio of the TMIn and TMGa flux with TMGa flux maintained at 10 µmol/min. TMIn flux is varied to change R. GaN is generally synthesized at 800 C- 900 C and InN at 550 C - 600 C. Hence, 700 C - 750 C range was of interest to attain 50-50 In-Ga content. Figure S3 is the plot of the indium content in the InGaN alloys at different combinations of temperatures and flux ratios.

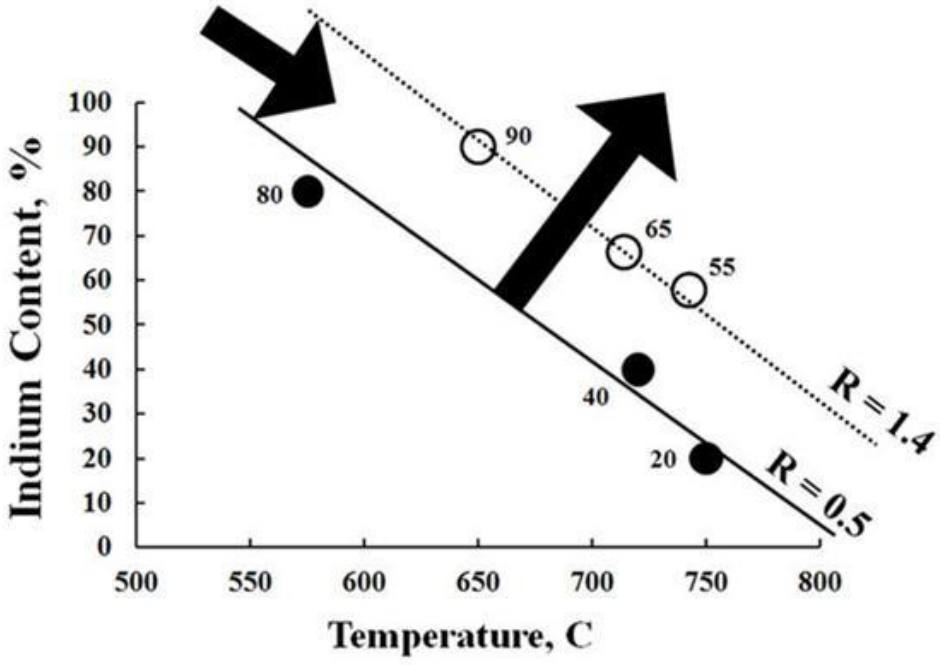


Figure S3: Plot of the indium content in InGaN alloys obtained with different sets of process parameters. R is the ratio of the TMIn/TMGa flow rates. At constant flux, indium content decreases with increase in temperature, due to the increased indium desorption at high temperatures. At constant temperatures, as R (indium/gallium flux ratio) is increased, indium content also increases.

MORPHOLOGY OF InGaN GROWTH ON GaN NANOWIRES

As described in the article text, orientation dependent growth of InGaN was observed on GaN nanowires. Formation of complete hexagonal shells of different thicknesses is clearly shown in figure S4.

On c-GaN nanowires

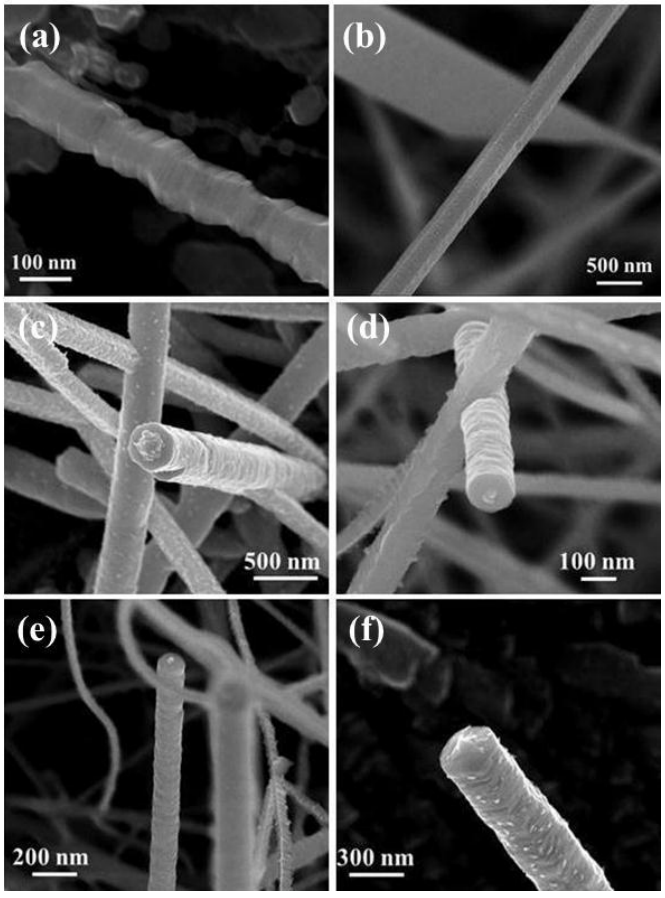


Figure S4: SEM images of the InGaN shell formation on various samples. The formation of a uniform hexagonal shell with the GaN wire protruding at the center.

On a-GaN nanowires

As shown already in figure 2 in the main article, growth is very different on a-GaN nanowires. The pyramids grow radially out from the two polar (0001) and (000-1) surfaces which is clearrly shown in figure S5a. The hexagonal shape of the pyramids is clear from the top view in figure S5b. The island coalescence into a shell bound by four facets is clear in figure S5c which also shows the hexagonal island at the tip. Finally, another perpective of the InGaN shell completely covering the GaN nanowire is shown in figure S5d.

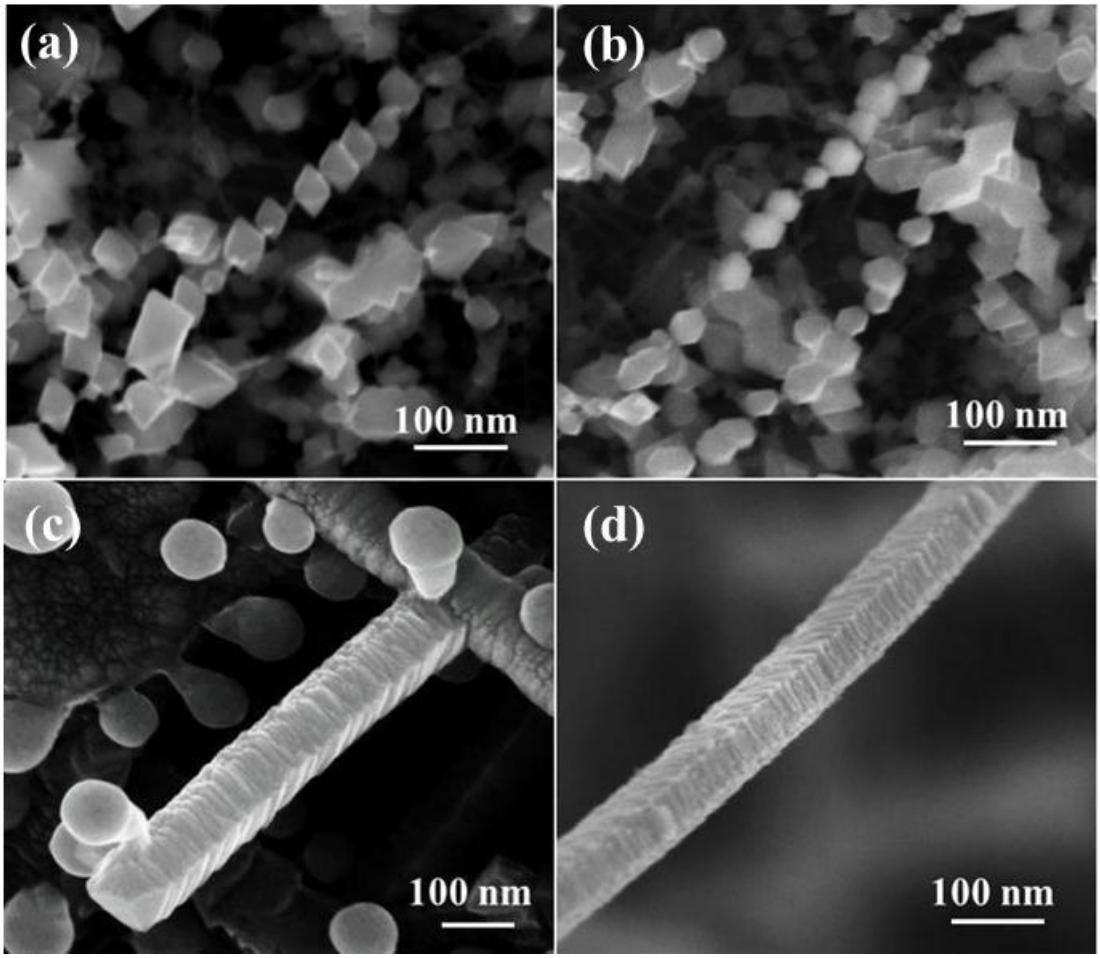


Figure S5: Perspective of the heteroepitaxial growth of InGaN on a-GaN nanowires. a) The pyramidal islands grow on the surface and not along the surface (for c-GaN nanowires) of the nanowire. The islands grow only on the two polar (0001) and (000-1) surfaces. b) Top view of the pyramids clearly shows the hexagonal shape of the islands. c) Side view of the growth of islands after coalescence clearly showing the coalesced pyramids forming a four faceted shell. d) InGaN shell on the nanowire.

DISTRIBUTION OF THE SPECIES IN InGaN LAYERS

Distribution of the species (gallium and indium) in the InGaN layers needs to be ascertained to determine the uniformity of the composition and show the lack of any phase segregation.

Figure S6 is the elemental map of InGaN growth on a-GaN nanowires showing the islands growing on the nanowires. GaN nanowire is clearly visible in the gallium map as the bright line and is conspicuously absent from the indium map. The maps clearly show the uniform distribution of the species in the alloy islands indicating the absence of phase separation.

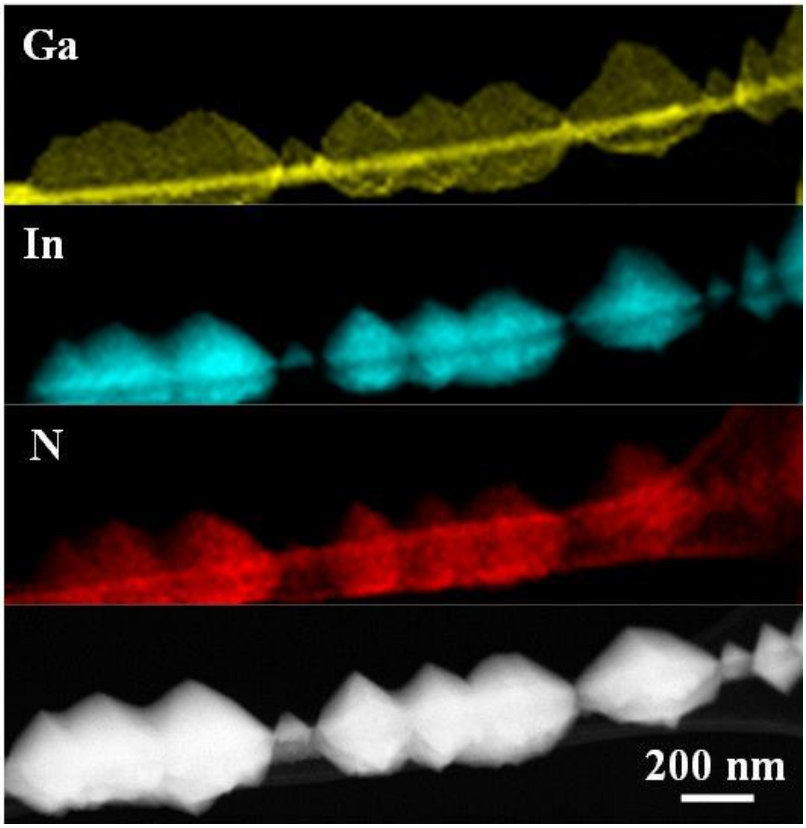


Figure S6: TEM EDS elemental map of InGaN growth on GaN nanowire. An image of the growth is also included for reference. The gallium and indium maps show uniform composition distribution without any phase segregation. Also, the GaN nanowire clearly shows up in the gallium map which should be and is absent from the indium map.

Figure S7 is the STEM EDS elemental map of InGaN growth on c-GaN nanowires. The partially coalesced islands can be seen aligned along the length of the nanowire. Similar to figure S6, the nanowire shows up in the gallium map. The material distribution is uniform in this case as well in the InGaN layers indicating the absence of any phase segregation.

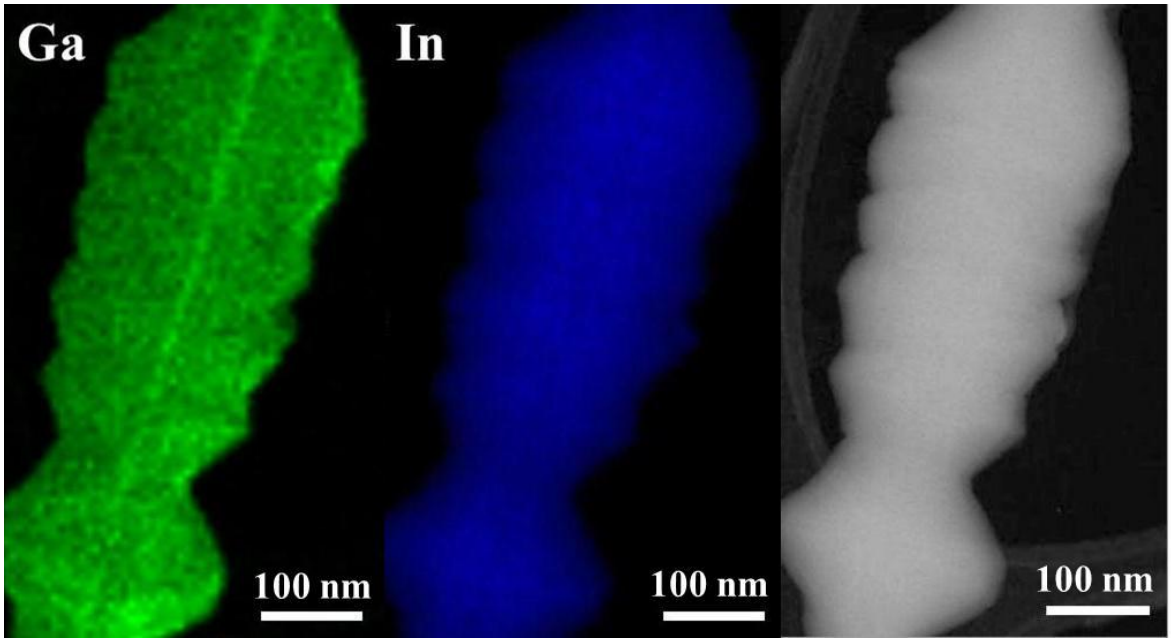


Figure S7: TEM EDS elemental map of InGaN growth on GaN nanowire. An image of the growth is also included for reference. The gallium and indium maps show uniform composition distribution without any phase segregation. Also, the GaN nanowire clearly shows up in the gallium map which should be and is absent from the indium map.

STUDY OF InGaN ISLAND NUCLEATION

According to the proposed growth mechanism, step nucleation and growth leads to the formation of islands at the very initial stage, followed by the growth of islands while maintaining a constant growth rate. Aspect ratio of islands of different sizes was measured for growth on a-GaN as well as c-GaN nanowires. This is indeed the observation as extremely small as well as large islands with the same aspect ratio have been observed as shown in figure S8.

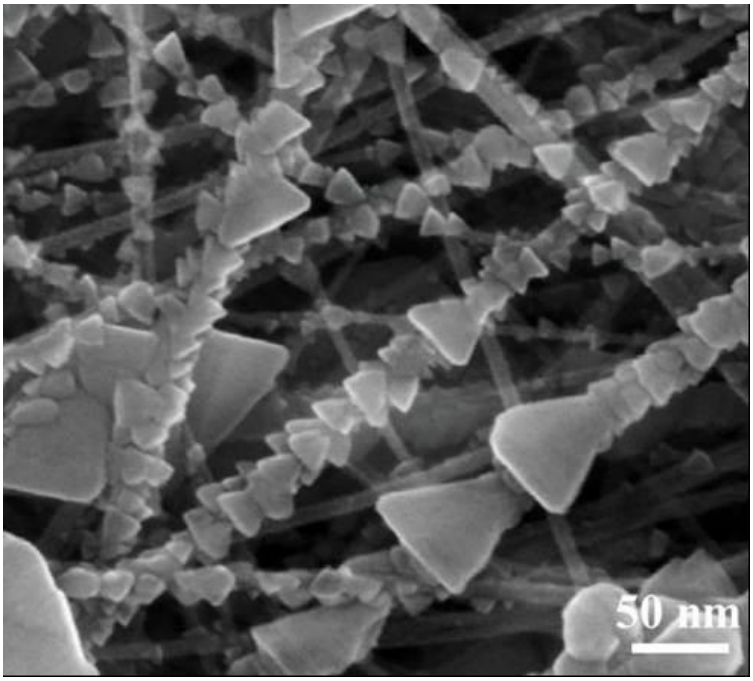


Figure S8: SEM micrograph of the InGaN growth on GaN nanowires. Islands with different sizes are shown indicating that the islands form at the very initial stages followed by the island growth at constant aspect ratio.

Wurtzite crystals have a characteristic c/a ratio of 1.63. However, looking from the top, the perspective correction has to be applied. As shown in the schematic S9, the height of the pyramid is the "c" and depending on the orientation of the base, it is either 1.73a or 2a. Hence, using the wurtzite c/a ratio, the measured height/base ratio in the two cases should be **0.94** (1.63/1.73) and **0.815** (1.63/2) respectively.

Figure S10 is the compilation of the height and base of the pyramids of different sizes measured on samples with different InGaN concentrations. The data in red is for the pyramids where two facets were visible which resulted in a 0.92 ratio and the data in black is for the pyramids where three facets were visible resulting in a ratio of 0.81 that agrees closely with the expected values.

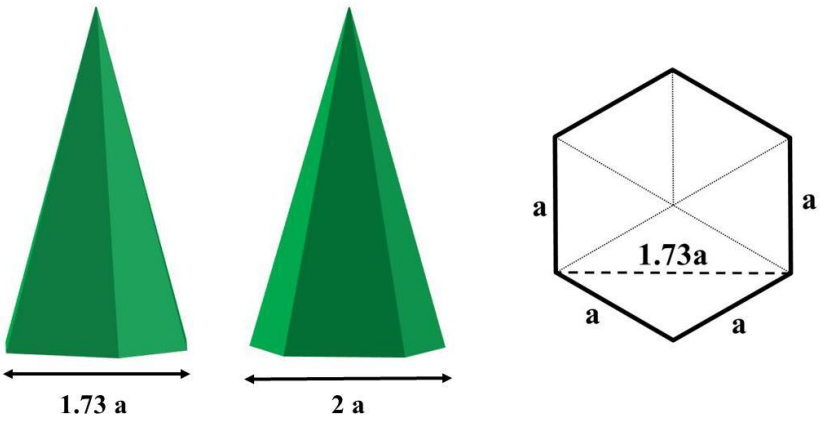


Figure S9: Schematic of the two possible views of the hexagonal pyramidal islands. The base is equal to 1.72 times the lattice constant "a" when only two facets are visible whereas the measured base would be twice the lattice constant "a" when three facets are visible.

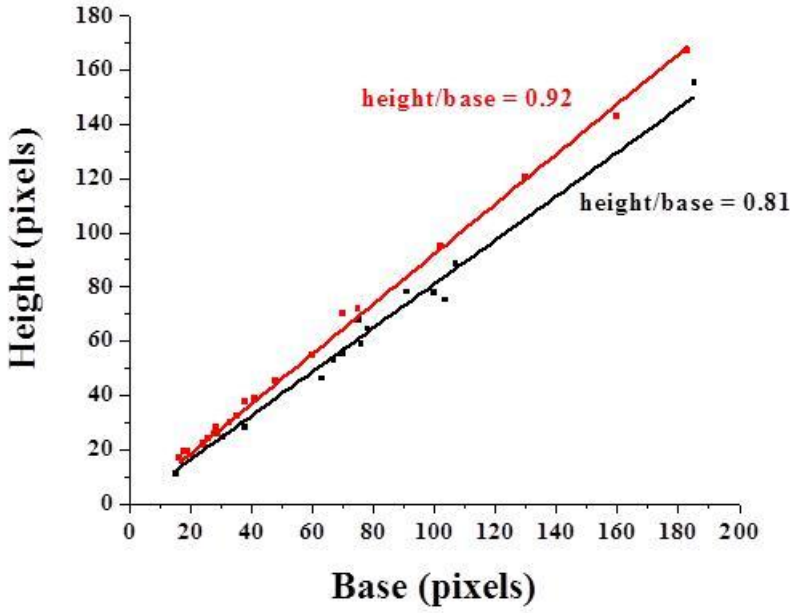


Figure S10: Aspect of the pyramidal islands of different sizes and different InGaN compositions. Number of facets of the pyramid visible in the plan view controls the ratio. The steps form a pyramidal shape at very initial stages and grow in size maintain the aspect ratio. The size of the pyramids has been measured from < 5 nm (smallest) to > 100 nm (largest), corroborating our proposed growth mechanism.

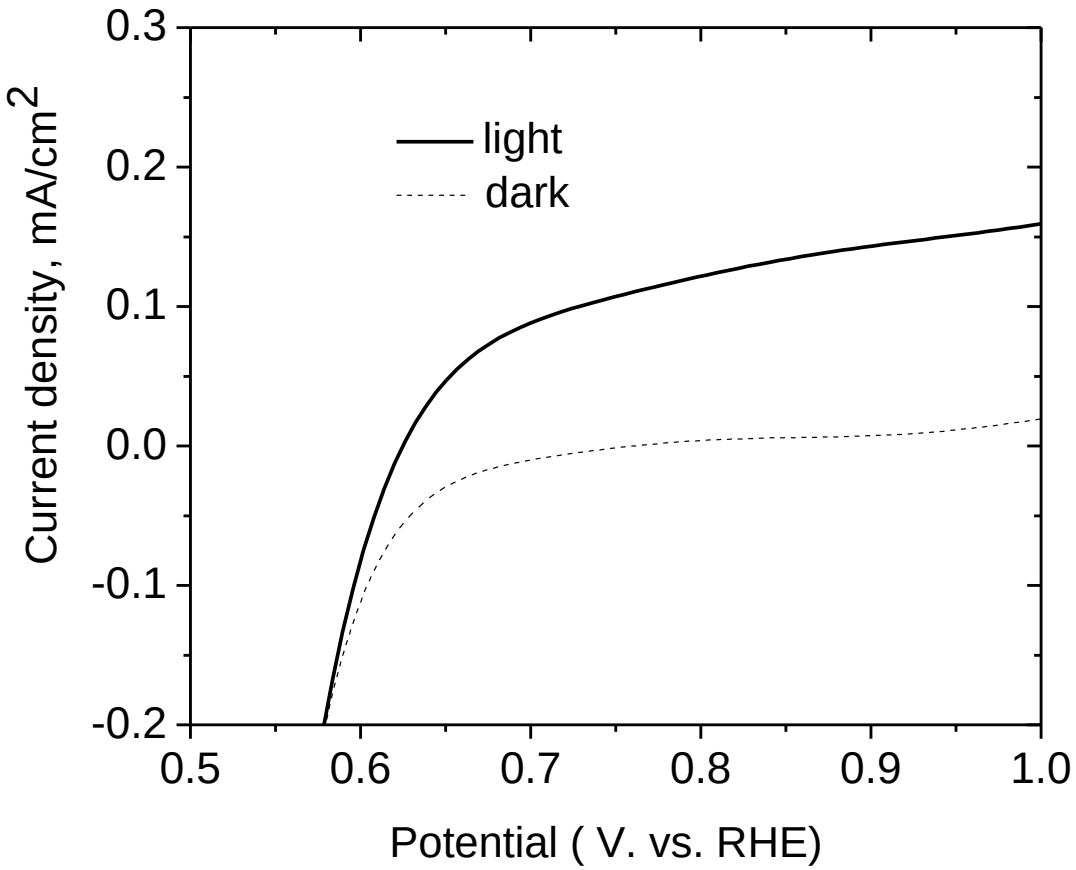
The observed trend and the consistent aspect ratio of the pyramidal islands indicate that the growth of the steps occurs at a constant velocity in the direction of the inclined (10-11) facet. This supports the proposed growth mechanism that step flow and growth forms the pyramids during very early stages of the growth.

PHOTOACTIVITY OF InGaN/GaN NANOWIRE STRUCTURES:

Photocurrent measurements:

A three electrode setup was used to measure the photocurrent of the InGaN/GaN nanowire structures. The working and counter electrodes are similar to the two electrode measurements and a Ag/AgCl reference electrode is also introduced in the system. A voltage sweep is made from -0.05V wrt OCP and 1 V while measuring the current.

The measurement is repeated in dark and under illumination (100 mW/cm^2 AM 1.5) to determine the photoactivity of the material as shown in figure S11. The photocurrent measurements on two different electrodes with similar InGaN growth showing the need for optimization of the back contact process. Photoactivity is observed in both cases but the current is an order of magnitude smaller in the second electrode.



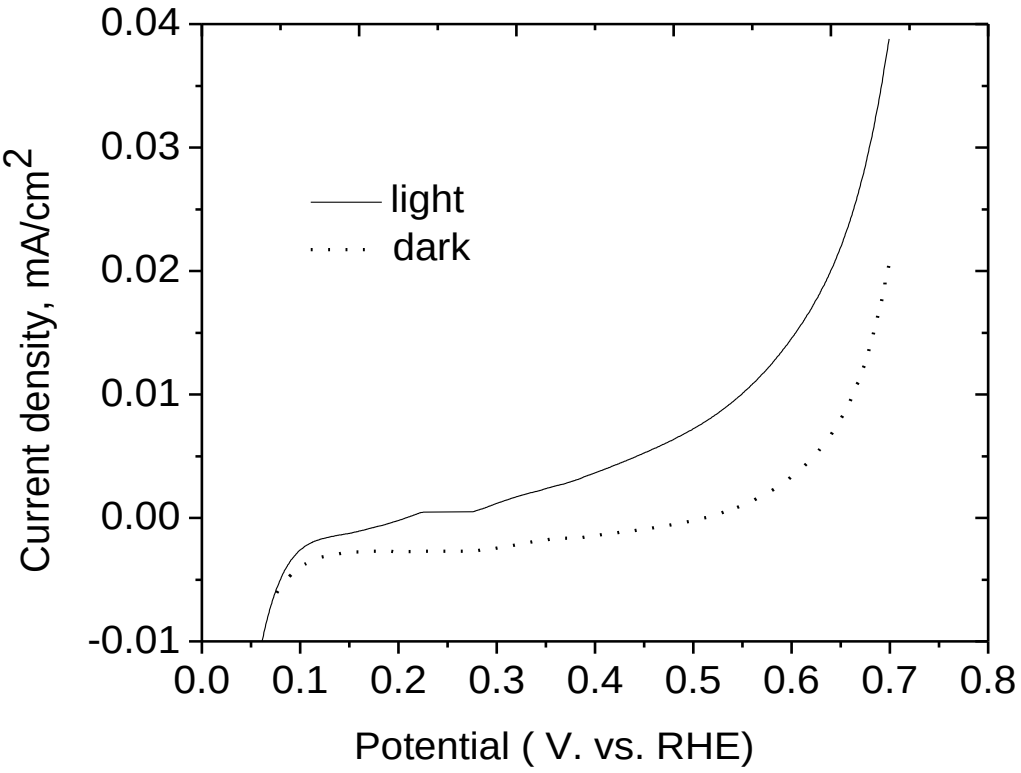


Figure S11: Photocurrent measurement on the InGaN/GaN electrode. Potential scan was performed from -0.05V vs OCP to 0.5 V at a scan rate of 25 mV/sec. Photocurrent onset occurs at about 0.1 V wrt Ag/AgCl. All the measurements were conducted at an illumination intensity of 100mW/cm^2

Stability of the electrodes

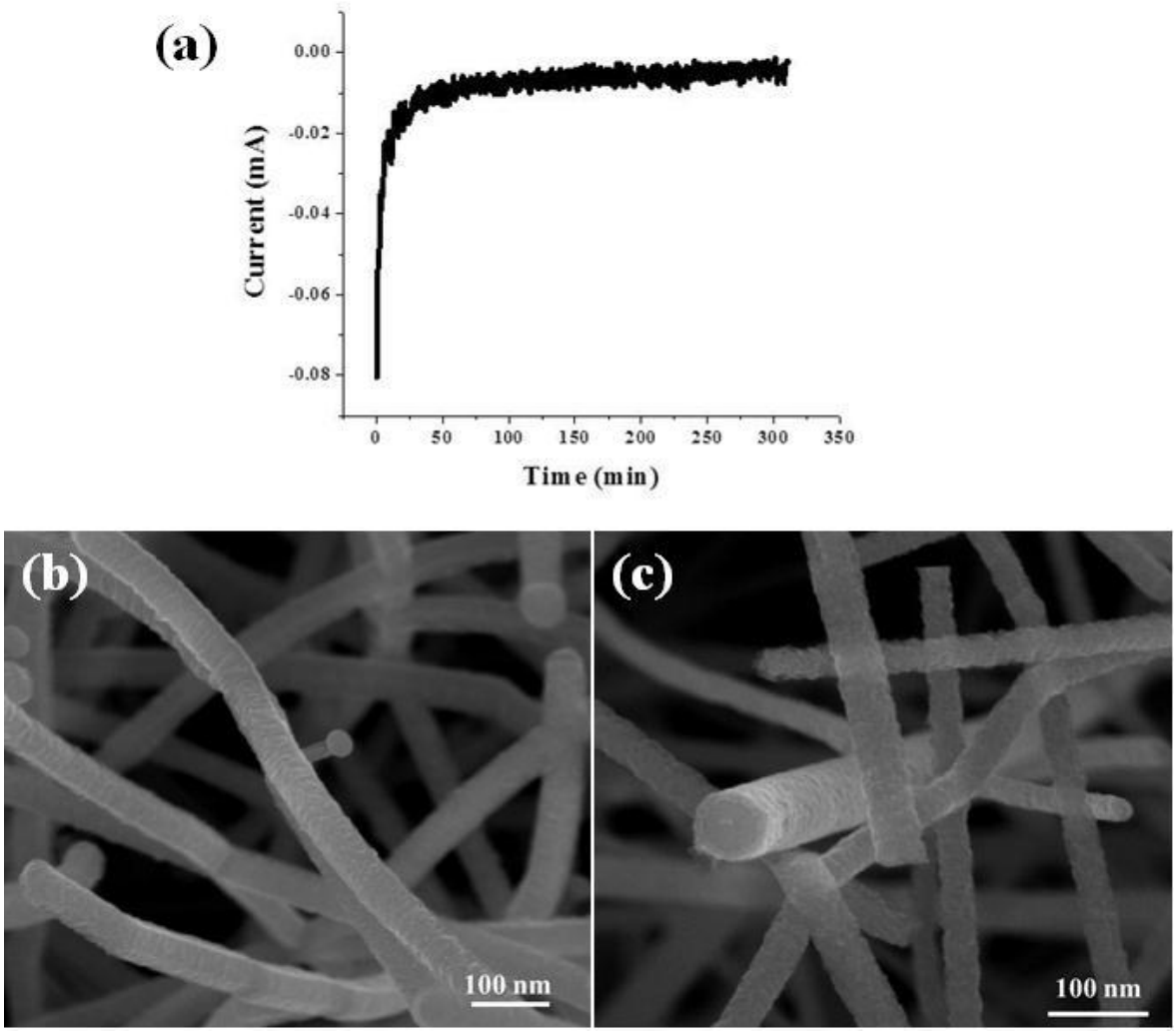


Figure S12: Stability measurements of the InGaN/GaN electrode measured at 0.5 V and 100 mW/cm^2 illumination. a) Photocurrent is measured on the second electrode which shows a fairly stable behavior. SEM images of the InGaN coating b) before and c) after the term photocurrent testing.

Stacking faults in GaN nanowires

Figure S13 shows the presence of stacking faults in c-plane GaN NWs.grown at typical growth temperatures of 750-850 ºC. Higher growth temperatures tend to result in stacking fault free GaN nanowires even with c plane oriented growth direction. However, the a-direction nanowires grown at the above growth temperatures of 750-850 ºC tend to be planar defect free. One issue is that the a-drection nanowires tend to grow fast leading to thin and long nanowires that are not ideally suitable for PEC applications. Efforts are currently underway to grow shorter a-direction nanowires and also stacking fault free c-direction nanowires and use them for growing InGaN layers for PEC testing.

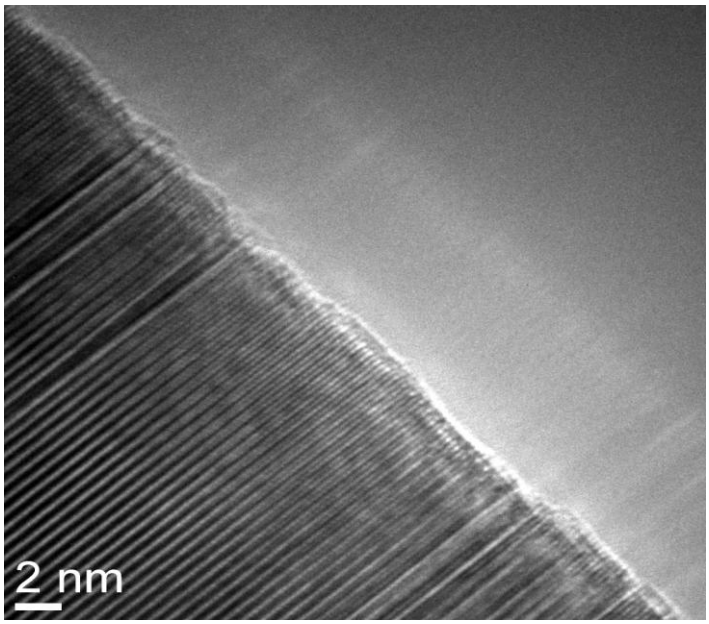


Figure S13: HRTEM image showing stacking faults in c-plane GaN NWs