On the Efficiency and Long-term Stability of MBE-grown III-Nitride Nanostructures for Unassisted Overall Water Splitting

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The direct conversion of sunlight to hydrogen via water splitting has emerged as one of the key technologies to achieve energy sustainability. Progress in this field, however, has been limited by the low photocatalytic efficiency of conventional metal-oxide materials. We have recently demonstrated that nearly defect-free GaN-based nanostructures can meet the thermodynamics for overall water splitting (OWS) [1]; and by tuning the surface Fermi-level through controlled Mg-dopant incorporation, the apparent quantum efficiency for solar-to-hydrogen conversion can be enhanced by nearly two orders of magnitude under UV [2] and visible light illumination [3-4]. In this work, we demonstrate multi-band InGaN nanosheet photochemical diode (PCD) structures, which can spontaneously induce charge carrier separation and steer charge carriers toward the distinct redox sites for water oxidation and proton reduction. During the synthesis of InGaN photochemical diode nanosheet structure, p-type dopant (Mg) concentrations are rationally tailored, which induces a large built-in electric field between the two parallel surfaces, schematically shown in Fig. 1a. Due to the presence of a net built-in potential ~300 meV (ΔE) along the lateral dimensión, as shown in Fig. 1b, the two surfaces are enriched with photo-generated holes and electrons to perform water oxidation and proton reduction reactions, respectively [5]. With spatially separated catalytic sites and reduced carrier recombination, the nanoscale PCDs exhibit stoichiometric H_2 and O_2 evolution, with a production rate of ~1.62 mmol $h^{-1}cm^{-2}$ and ~0.784 mmol $h^{-1}cm^{-2}$, respectively, which is equivalent to a solar-to-hydrogen efficiency over ~3%. We are currently developing novel III-Nitride nanostructured device on Si, which can demonstrate unprecedented performance stability for more than ~580 hours in photochemical water splitting reaction when the surface is modified with suitable co-catalyst nanoparticles. With structural engineering, we aim to enhance solar-to-hydrogen efficiency in the range 5-10%.

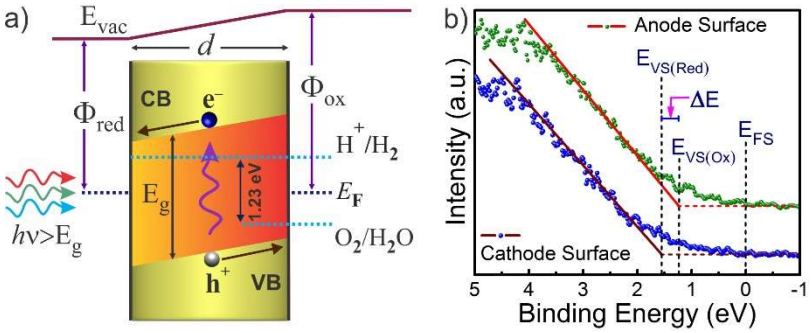

Figure 1: a) Energy-band representation of proposed photochemical diode (PCD) with radial thickness *'d'*, showing built-in electric field (band-bending) that separates the charge carriers (electron and hole) and drives towards opposite cathode and anode surfaces. b) ARXPS valence spectrum for cathode and anode surface of *p*-InGaN PCD nanosheets, depicting the offset in surface valence band maximum (E_{VS}) relative to surface Fermi-level (E_{FS}).

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[1] D. Wang *et al., Nano Lett.* **11** (6), 2353 (2011). [2] M. G. Kibria *et al., Nat. Commun.* **5**, 3825 (2014).
[3] F. A. Chowdhury *et al.*, *APL Mater.* **3**, 104408 (2015). [4] M. G. Kibria *et al., Nat. Commun*. **6**, 6797 (2015).
[5] F. A. Chowdhury *et al., Nat. Commun*. **9**:1707 (2018).

Supplementary Information:

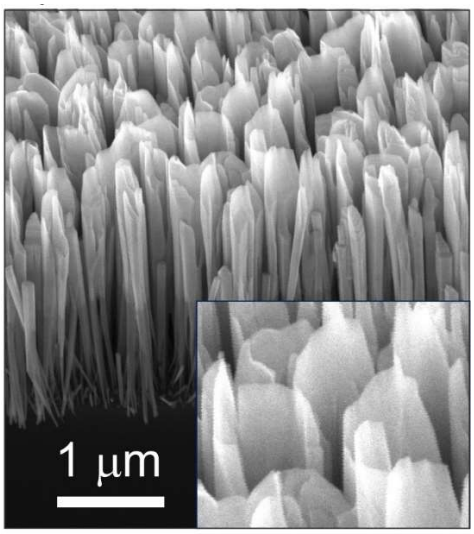

Figure 2: A 45° tilted SEM image of InGaN:Mg PCD nanostructures, vertically aligned on Si substrate. Scale bar, 1 µm. The magnified image of the nanosheets is also presented in the inset for clarity.

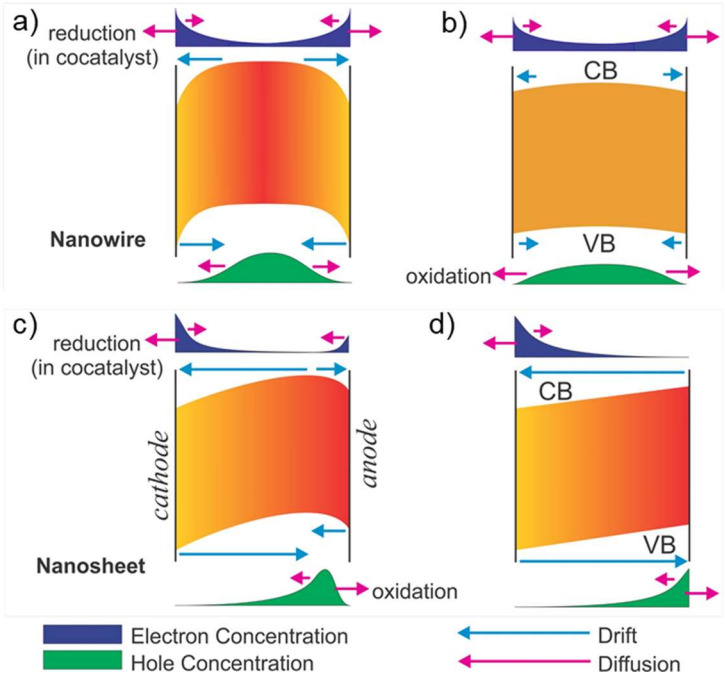

Figure 3: a) Optimally doped nanowire provides carrier separation in *near-surface* region under low excitation, however, with low photocatalytic activity due to trapping of photo-generated holes in the bulk. b) Under concentrated irradiation, reduced band-bending in nanowire lowers the hole-diffusion barrier for water oxidation, the rate-limiting step for overall water splitting. Carrier transport mechanism in a photochemical diode nanosheet under c) low excitation and d) concentrated high excitation. Built-in potential and associated band bending due to Mg-doping gradient plays critical role in carrier separation, thereby suppressing charge carrier recombination in both the bulk and surface region.

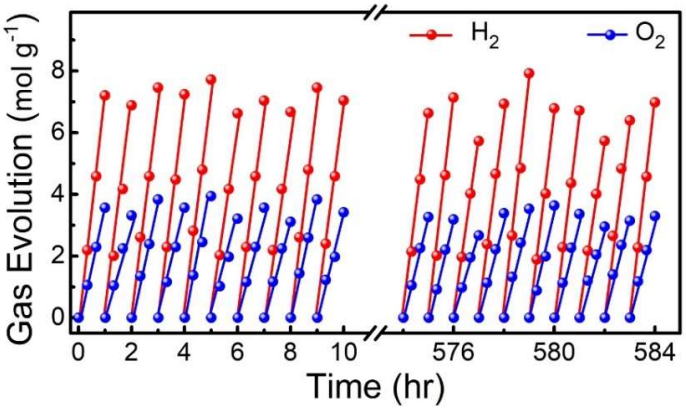

Figure 4: Repeated time evolution of H_2 and O_2 production from first and last 10-cycles among 584-cycles of unassisted overall (neutral pH) water splitting, using GaN/InGaN nanowires, decorated with both oxidation and reduction co-catalysts (Co_3O_4 and Rh/Cr_2O_3, respectively). Average rate of H_2 and O_2 production (7.14 and 3.54 mol $h^{-1}g^{-1}$, respectively) from each cycle during long-term repeated course of water splitting under concentrated sunlight illumination, demonstrating excellent performance and stability of the device (area of ~3 cm^2 and active GaN/InGaN catalyst mass of ~0.48 mg).