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doi:10.1017/S1431927618008838
Microsc. Microanal. 24 (Suppl 1), 2018
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Hierarchical InGaN Nanowires for High-Efficiency Solar Water Splitting

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Solar water splitting has become a promising way to alleviate supply instability of solar energy by directly storing energy in the form of hydrogen fuel. Maximizing efficiency for photoelectrochemical (PEC) water splitting requires (i) a tunable bandgap that captures the solar spectrum, (ii) an energy band edge that spans the water redox potential, and (iii) high quantum efficiency [1,2]. Although a variety of materials such as Si, Ta_3N_5, and $BiVO_4$ have been studied as photoelectrodes, most materials have not yet fulfilled these requirements. For instance, the onset potential of Si and Ta_3N_5 is too large so charge carriers cannot be sufficiently generated under sun illumination and $BiVO_4$ has a wide 2.4 eV bandgap that limits the efficient utilization of the solar spectrum [1,2]. The InGaN ternary system is an optimal photoelectrode for efficient solar hydrogen production (Fig. 1a). The bandgap (E_g) of InGaN is direct and tunable from 3.4 (GaN) to 0.65 eV (InN) for indium compositions up to ~50%, allowing optimal use of the entire solar spectrum ($E_g \approx 1.7$ eV), which could potentially enable a solar-to-hydrogen efficiency over 25% [1,2,3]. However, creating high-performance InGaN photoelectrodes is difficult as In-rich crystals are highly strained causing phase segregation and subsequent performance degradation.

Here we show low-dimensional nanostructures accommodate crystalline InGaN nanowires capable of enhanced water splitting performance (highest reported value of 10.9 mA/cm^2 at 1.23 V versus reversible hydrogen electrode (RHE)) and photoluminescence (a single emission peak at 720 nm) [2]. Using plasma-assisted molecular beam epitaxy (MBE), highly crystalline InGaN can be grown as one dimensional (1D) nanostructures. This allows high quantum efficiency with a larger surface area for PEC reaction [2,4]. Cross-sectional electron microscopy of InGaN/Si (Fig.1b, c) reveals that the crystalline InGaN nanowires have an approximate height of ~700 nm tall and diameter of ~200 nm wide which extend atop a polycrystalline growth layer on the Si substrate. The low-dimensional geometry not only allows high In concentrations, but also provides more catalytically active surface area. IrO_2 co-catalysts with a size of 1-2 nm were uniformly loaded on the InGaN surface (Fig. 1c) to further enhance performance. The current-potential (J-V) curves of IrO_2 (Fig.1d) show that the photocurrent density of IrO_2/InGaN reaches 10.9 mA/cm^2 at 1.23 V versus RHE due to the lower onset potential of the IrO_2 co-catalyst combined with the sufficient InGaN bandgap of ~1.7 eV. The maximum applied bias photon-to-current efficiency (ABPE) of the IrO_2/InGaN photoanode calculated from the J−V curve is 3.6%, which is the highest among those of previously reported photoelectrodes [2].

InGaN crystals can also be grown with hierarchical order that spans the nano- to atomic- scale through 1D lithographic templating (Fig. 2a-c). Cross-sectional electron microscopy shows the periodic GaN nanowalls (width ~500 nm, height ~1 um, spacing ~400 nm) that template confined InGaN growth (Fig. 2a). InGaN grows as triangular prisms atop each nanowall (Fig. 2a) because the polar facet (001) has a faster growth rate than that of the semi-polar (101) and non-polar (100) facet sidewalls. It is also interesting that a sharply faceted single crystal InGaN nanoridge (~50 nm width) forms along the top of each nanowalls (Fig. 2c). In confined geometry heteroepitaxy, increased In incorporation can occur due to

https://doi.org/10.1017/S1431927618008838 Published online by Cambridge University Press

the onset of 'strain relaxed growth' [4]. An energy dispersive x-ray (EDS) map shows that the InGaN nanoridge is composed of Ga, In, and N without phase segregation (Fig. 2b). Atomic resolution dark field STEM reveals a lattice spacing of 2.95Å (Fig. 2e) and confirms an In-rich InGaN crystal (InN spacing is 3.06 Å). Lastly, the highly ordered 1D InGaN provides strong photoluminescence emission (Fig. 2d).

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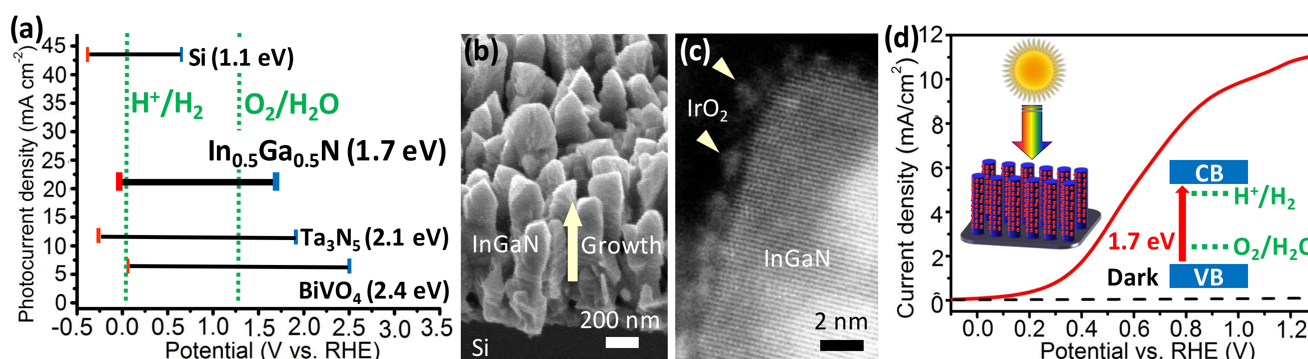

Figure 1. InGaN nanowires with IrO_2 nanoparticles provide enhanced water splitting (a) The maximum theoretical photocurrent densities of different photoanode materials under AM 1.5G 1-sun illumination. (b) Side-view SEM reveals epitaxial growth of IrO_2-InGaN nanowires across a silicon wafer. (c) A cross-sectional high-angle annular dark field (HAADF) STEM image shows the ~1-2 nm IrO_2 nanoparticles adsorbed to the InGaN surface. (d) J-V curves of InGaN and IrO_2/InGaN in 0.5 M H_2SO_4 under AM 1.5G 1-sun illumination.

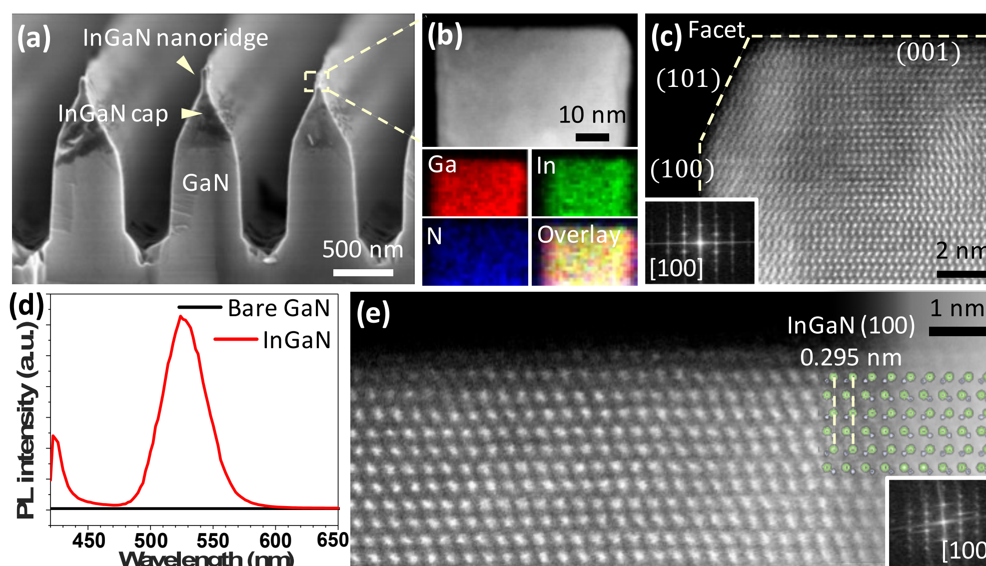

Figure 2. Single crystal 1D InGaN nanoridge grown on GaN wall (a) Side-view SEM (b) HAADF STEM image on cross-sectional InGaN nanowalls and simultaneous STEM EDS spectroscopic mapping showing the grown InGaN tip primarily comprised of Ga (red), In (blue), and N (green). (c) High resolution HAADF STEM on the sharply-faceted InGaN nanoridge in c indicating highly single crystalline. (d) Room temperature micro-PL of InGaN nanowalls and reference GaN wall. (e) Atomic resolution HAADF STEM on the termination of the InGaN tip in c indicating the lattice constant that is consistent with InGaN.

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