MATERIALS SCIENCE

Special Topic: Quantum Physics and Devices of Quantum Dots

**InN/InGaN quantum dot electrochemical devices: new solutions for energy and health**

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**ABSTRACT**

A review is given of the exceptional electrochemical performance of epitaxial InN/InGaN quantum dots (QDs) as photoelectrodes for solar hydrogen generation by water splitting, as biosensor transducers and as anion-selective electrodes, and they are also evaluated as supercapacitor electrodes. The performance is benchmarked against the best performances of other reported materials and nanostructures. A model based on the unique interplay of surface and quantum properties is put forward to understand the boost of catalytic activity and anion selectivity interlinking quantum nanostructure physics with electrochemistry and catalysis. Of equal impact is the direct growth on cheap Si substrates without any buffer layers, allowing novel device designs and integration with Si technology. This makes the InN/InGaN QDs viable, opening up new application fields for III-nitride semiconductors.

**Keywords:** quantum dot, solar hydrogen, biosensor, ion-selective electrode, supercapacitor, InN, InGaN

**INTRODUCTION**

The traditional applications of epitaxially grown semiconductor heterostructures and related quantum structures, quantum wells, quantum wires and quantum dots (QDs) are optical and electrical devices. But there is another, basically unexplored class of devices with huge, actually much wider, application areas of great variety, including the economically and societally most relevant fields of energy and health: electrochemical devices. InGaN is the electrode material of choice for these devices. InGaN is chemically stable, non-toxic, bio-compatible, and has a wide direct bandgap tunability and high absorption coefficient and carrier mobility. The industrial mass production is in place for LEDs. InGaN fulfills all necessary requirements, outperforming other semiconductor, metal-oxide, polymer and carbon-based materials. A number of studies of InGaN planar layers, porous, patterned and columnar structures used as electrochemical electrodes have been reported [1–10].

Here, a review is given of the exceptional performance of epitaxial InN/InGaN QDs as electrode materials for electrochemical devices. The performance is explicitly measured against the best reported performances of other materials and nanostructures. None of them is QD-based. More generally, for electrochemical device applications, nanostructured materials are made almost exclusively by chemical-synthesis routes. Nanomaterials exhibit porous structures, foams, tissues, nanowires and colloidal nanoparticles. However, it is not the aim to review such materials, electrochemical electrodes and devices. The purpose is to present the application of QDs. Epitaxial InN/InGaN QDs are a new player in the field. They combine physical synthesis routes of epitaxial heterostructure nanomaterials with chemical device applications. The variety and performances are great in a truly interdisciplinary setting.

First, three ‘killer’ applications are discussed: (i) photoelectrodes for photoelectrochemical hydrogen generation by water splitting for solar-energy harvesting and storage; (ii) enzymatic biosensors for the detection of glucose and cholesterol for medical diagnostics; and (iii) anion-selective electrodes, also evaluated as supercapacitor electrodes. Second, the epitaxial growth of InN/InGaN QDs and InGaN...
layers over the entire composition range on Si substrates is addressed. It enables minimized cost and integration with Si technology. In particular, the direct growth on Si without any electrically insulating buffer layers opens the door for novel device designs. Finally, a model for the superior electrochemical performance of the InN/InGaN QDs is developed. The model is based on the unique surface and quantum properties of the InN QDs. The model describes the interplay of the intrinsic positive surface charge and the zero-dimensional electronic states. It provides a basic understanding of the boost in catalytic activity and anion selectivity.

Depicted in Fig. 1a is a scheme of the InN QDs grown on a compact, In-rich InGaN layer on a Si (111) substrate. In Fig. 1b, an atomic force microscopy (AFM) image of the InN QDs on the In-rich InGaN layer with 54% In content is shown. Growth is performed by a plasma-assisted molecular beam epitaxy (PA-MBE). The PA-MBE machine is equipped with a radio frequency (RF) plasma source for activated nitrogen supply and standard Knudsen cells for elemental Ga and In supply. Typical growth conditions are: growth temperature of ~450°C, growth rate of ~0.5 μm/h for InGaN, InGaN layer thickness between 50 and 450 nm, InN amount for QD formation of one to three monolayers and V-to-III flux ratio close to stoichiometric, slightly nitrogen-rich. The photoluminescence (PL) spectra of the InN/InGaN and InAs/GaAs QDs are basically identical [11]. The difference is the 10 times larger absorption and the much higher carrier mobility of InGaN. This motivates replacing InGaAs by InGaN for optical—and possibly electrical—devices. Maximized sensitivity and efficiency can be expected for photodetectors and solar cells, in particular intermediate-band solar cells [14]. Any device harvesting solar energy will benefit.

SOLAR HYDROGEN GENERATION BY WATER SPLITTING

Increasing world energy consumption and greenhouse-gas emission are very dangerous societal threats. Innovative, clean and renewable-energy sources are urgently needed to replace fossil fuels. Solar hydrogen generation by water splitting, coined artificial photosynthesis, is identified as a prime solution. Solar energy is directly stored as chemical energy—solar fuel. This solves the electrical-energy storage problem of photovoltaics and other renewable-energy sources. The problem is to find efficient and stable materials.

Two main routes are pursued. Wide-bandgap metal-oxide photoelectrodes are used for direct photoelectrochemical water splitting or photocatalyst cells for water electrolysis [15,16]. Solar-to-hydrogen efficiencies of 14% were achieved by
InGaN is chemically stable. The bandgap energy can be tuned to the optimum value of 1.6–1.7 eV by adjusting the In content to 45–55%. This bandgap energy is high enough to drive the water-splitting reaction $V_{\text{redox}} = 1.23 \text{ V}$ and low enough so that most of the solar radiation is absorbed. Very importantly, too, the conduction band edge and valence band edge straddle the redox potentials of $(\text{O}_2/\text{H}_2\text{O})$ and $(\text{H}^+/\text{H}_2)$. This is prerequisite for the direct photoelectrochemical hydrogen production [20]. No additional surface functionalization (co-catalyst, sensitizer) is then needed, which reduces absorption.

An In$_{0.54}$Ga$_{0.46}$N layer photoanode with the ideal bandgap energy drives photoelectrochemical water splitting and hydrogen generation without external voltage. When functionalized with InN QDs on top, the efficiency is more than doubled [21]. The measurements of the incident photon-to-electron conversion efficiency (IPCE) are performed in a three-electrode configuration with the InN/InGaN QD or InGaN layer working electrode, an Ag/AgCl reference electrode and a Pt counter electrode. The electrodes are immersed in a pH 3 H$_2$SO$_4$ plus 0.5 M Na$_2$SO$_4$ aqueous electrolyte solution. Illumination is by a 1000-W Xenon arc lamp through band pass filters. The incident power densities are 93–98 mW/cm$^2$ for each filter.

Figure 2a shows the IPCE of the InN/InGaN QD and InGaN layer photoanodes as a function of wavelength. The IPCE is defined as the percentage of electrons taking part in the redox reaction (determined from the photocurrent density) versus the number of incident mono-chromatic photons (determined from the wavelength-dependent incident power density), according to:

$$\text{IPCE} \, (\%) = \frac{1240 \, (\text{V nm}) \times \text{photocurrent density} \, (\text{mA/cm}^2)}{\text{incident light wavelength} \, (\text{nm})} \times \left(\frac{\text{light intensity} \, (\text{mW/cm}^2)}{100}\right)^{-1}.$$

![Figure 2](https://example.com/figure2.png)

**Figure 2.** (a) IPCE spectra of the InN/InGaN QD, InGaN layer and GaN photoelectrodes as function of wavelength at 0.0, 0.5 and 1.0 V versus the Ag/AgCl reference electrode. (b) Hydrogen and oxygen evolution after eight hours per illuminated area as a function of wavelength at zero externally applied voltage versus the Pt counter electrode for the InN/InGaN QD and InGaN layer photoelectrodes (redrawn from [21]).
The IPCE between 450 and 750 nm is clearly due to the InGaN layer—there is no response from GaN, shown for reference. Thanks to the optimum InGaN bandgap energy, the response captures the peak irradiance of solar radiation. The IPCE values for the InN/InGaN QDs are larger by a factor of about 2.3 than those for the InGaN layer. The IPCE values increase with voltage versus the Ag/AgCl reference electrode and are reaching a maximum of 77% for the InN/InGaN QDs at 1 V.

The evolution of hydrogen and oxygen directly correlates with the IPCE. The measurements of the hydrogen and oxygen evolution are performed in a two-electrode configuration with the InN/InGaN QD or InGaN layer working electrode and Pt counter electrode. No external voltage is applied. The amount of hydrogen and oxygen is measured by a gas chromatography analyser. The evolution is shown in Fig. 2b as a function of wavelength after eight hours of illumination. Hydrogen bubbles are clearly observed on the Pt counter electrode during illumination.

The hydrogen evolution for the InN/InGaN QD photoanode over a time duration of eight hours is shown in Fig. 3a. The theoretical hydrogen evolution is calculated from the photocurrent according to Faraday’s law of electrolysis. The measurement is again performed in a two-electrode configuration, now under white-light illumination. The incident power density is 100 mW/cm², the same as that of solar radiation. No external voltage is applied. The hydrogen evolution is very stable, confirming the good chemical stability of the InN/InGaN QD photoanode. The theoretically deduced and experimentally measured hydrogen-generation rates per active area amount to 86 and 81 μmol/h1/cm². The faradaic efficiency is 94%.

The corresponding photocurrent density measured over time is shown in Fig. 3b. It is likewise very stable. The photocurrent density amounts to almost 5 mA/cm². This current density j and the incident light power density P determine the solar-to-hydrogen power conversion efficiency η:

\[
\eta = \frac{j \times 1.23V}{P}.
\]

The solar-to-hydrogen efficiency is deduced correctly here. Measurements are performed in a two-electrode configuration with zero externally applied voltage and proven (almost) 100% faradaic efficiency [22]. The solar-to-hydrogen efficiency amounts to 6%. For an externally applied voltage of only 0.2–0.3 V, the applied bias photon-to-current efficiency, deduced from the photocurrent versus voltage curve [21], rises to close to 20%. The corresponding solar-to-hydrogen efficiency then rises to above 20% when the bias is provided by a solar cell. These high solar-to-hydrogen efficiencies for a single photoanode have to be seen in relation to the best reported ones. The nanoporous BiVO₄ photoanode has an efficiency of 1.72% for an applied voltage of 0.6 V versus RHE [18]. A GaN/InGaN nanowire photoanode has 1.8% efficiency under 26 suns concentrated sunlight. The efficiency reduces to below 0.3% for 1 sun [10]. For the high efficiency of the InN/InGaN QD photoanode, InGaN layers with a thickness of only several 10 nm suffice. This is due to the high absorption coefficient, saving fabrication cost and raw materials.

**BIOSENSORS**

Biosensors have a huge variety of applications of the highest societal and economic impact. Applications include medical diagnostics (point-of-care and home), environmental monitoring (most relevant for water and air), food analysis, industrial process control and biodefense. Nanomaterial-based biosensors basically exclusively employ colloidal metal, semiconductor and magnetic nanoparticles as well as nanonostructured carbon [23]. Among such nanomaterial-based biosensors, colloidal semiconductor QD biosensors use optical readout schemes based on the luminescent properties of the QDs [24–26]. Compared to optical or other sensing techniques, enzymatic electrochemical biosensing is conceptually robust, fast, simple to use on-site and cheap.

An electrochemical biosensor consists of three elements: (i) the bioreceptor, selective for the target analyte, catalysing a specific biochemical reaction; (ii) the transducer, which transforms the biochemical reaction of the analyte with the bioreceptor into an electrical signal; and (iii) the electronic system, amplifying and displaying the signal. The use
of InN/InGaN QDs as transducers in biosensors is a radical turn from the established approaches. It is motivated by the search for ever better transducer materials in terms of biosensor sensitivity, response time, stability, repeatability and reusability.

The decision is for potentiometric sensing. The potential difference or electromotive force (EMF) between the InN/InGaN QD working electrode and an Ag/AgCl reference electrode is measured. This potential difference is proportional to the logarithmic analyte concentration, according to the Nernst equation. The decision for potentiometric sensing is because the EMF is insensitive to the sensor area. No additional power supply is required, in contrast to amperometric sensing techniques. The most simple and robust sensing method is adopted. Also, the electrode fabrication is easy, as there are no stringent requirements on the electrode area. The biosensor chosen for performance demonstration is a glucose biosensor for medical diagnostics [27]. This is because it is the most widespread of all types of biosensors. Moreover, historically, it is the first described biosensor and it is the first commercial one. The biosensors InN/InGaN QD transducers are functionalized with glucose oxidase, an enzyme catalysing the oxidation of glucose. The glucose oxidase is protected by a Nafion membrane. The bio-compatibility of InGaN preserves high enzymatic activity. The InN/InGaN QD biosensor exhibits excellent linearity, sensitivity, response time, stability, repeatability, reusability and selectivity.

Figure 4a depicts the EMF of the InN/In0.54Ga0.46N QD biosensor as a function of the logarithmic glucose concentration in the range from $1 \times 10^{-5}$ to $1 \times 10^{-2}$ M. Exp. #1–3 denote three repeated experiments, showing good reproducibility. The EMF is linear versus the logarithmic glucose concentration over the wide concentration range. The sensitivity is 80 mV/decade. This is significantly larger than the theoretical limit given by the Nernst equation of 59 mV/decade at room temperature. The response time when dipping the InN/InGaN QD biosensor into the 500 μM glucose solution is shown in Fig. 4b. The response time after which the EMF is stable within 0.5% is less than two seconds. The time response of the bare InGaN layer is shown in the inset of Fig. 4b for comparison. It is much slower. The EMF is much lower and not stable in time.

The InN/InGaN QD biosensor exhibits excellent storage stability and reusability. This is evidenced by a series of repeated experiments for 14 consecutive days, shown in Fig. 5a. Besides some fluctuations, the EMF measured here for a 500-μM glucose solution shows no systematic changes. The selectivity of the biosensor is tested for two common interfering agents: ascorbic acid and uric acid. Upon adding 50 μM ascorbic acid or uric acid to the 500-μM glucose solution, the EMF does not change substantially, shown in Fig. 5b. The selectivity is provided by the specific enzyme and not primarily by the InN/InGaN QD transducer.

An InN/InGaN QD biosensor for the detection of cholesterol has also been fabricated. Cholesterol oxidase is used as the enzyme. The sensitivity of this biosensor is 96 mV/decade and the response time is again less than two seconds [28]. This has to be compared with the performance of best reported transducers. The sensitivity of a ZnO nanowall biosensor is 53 mV/decade with five seconds response time [29]. A ZnO nanorod biosensor reveals 35 mV/decade with 10 seconds response time [30]. Besides, ZnO is not stable in water.

**ANION-SELECTIVE ELECTRODES AND SUPERCAPACITORS**

Ion-selective electrodes are used as sensors for measuring ionic concentrations in analytical chemistry and biochemical research. They find wide
Figure 6. (a) EMF of the InN/InGaN QD anion-selective electrode as a function of the logarithmic NaCl concentration ranging from 1 mM to 1 M. Exp. #1–3 denote three different experiments. (b) CV curves of the InN/InGaN QD (red) and InGaN (black) anion-selective electrodes in 0.1 M KCl aqueous electrolyte. The scan rate is 20 mV/s (redrawn from [37,38]).

applications in research as well as in industrial process control, physiological measurements and environmental monitoring [31–35]. Usually, ion-selective electrodes are membrane electrodes. The membrane is permeable for a specific ion, so an electric potential difference builds up across the membrane. At equilibrium, this potential difference is proportional to the logarithmic concentration/activity of the ion in the solution, according to the Nernst equation. The potential difference across the membrane cannot be measured directly. The electrode potential is measured relative to the potential of a reference electrode. This establishes a potentiometric sensor [31–35]. Amperometric sensing is also possible [36].

The anion-selective nature of the epitaxial InN/InGaN QDs is of different origin. The pronounced potentiometric [37] and amperometric [38] signals originate from active attraction and attachment of anions to the QDs. Figure 6a shows the EMF of the InN/InGaN QD electrode as a function of the logarithmic chloride ion concentration in NaCl aqueous solution [37]. The choice for chloride ions as target ions is due to their importance in measuring the salinity of water or the salt content in food. Chloride ions control fundamental processes in cells. Their monitoring is highly relevant to prevent many diseases.

The measurement setup comprises the InN/InGaN QDs as working electrode and an Ag/AgCl reference electrode. The EMF is linear versus the logarithmic chloride ion concentration in the measured range from 1 mM to 1 M. Repeated experiments (denoted Exp #1–3) show reproducible results. The sensitivity is 96 mV/decade, which is far above the theoretical limit set by the Nernst equation. No membrane electrode was found to beat this limit. Among the best solid-state electrodes, an InN thin film showed a sensitivity of 47 mV/decade with several 10 seconds response time. The response time of the InN/InGaN QD electrode is less than two seconds. After that, the EMF is very stable and repeatable.

In pH buffer solutions with pH values of 2–7, no clear response to cations is detected. The EMF is much smaller but still negative due to the presence of anions in the solution. This underlines the selectivity for anions. The InN/InGaN QD electrode also exhibits excellent storage stability, as evidenced by a series of repeated experiments for 10 consecutive days. They show no systematic changes of the EMF. The electrode can be used for a long time, retaining its high sensitivity and fast response.

Figure 6b depicts the cyclic voltammetry (CV) curves performed at a scan rate of 20 mV/s for the InN/InGaN QDs and the bare InGaN layer in 0.1 M KCl aqueous electrolyte [38]. The measurements are carried out in a three-electrode configuration with the InN/InGaN QD or InGaN layer working electrode, the Ag/AgCl reference electrode and Pt counter electrode. As required for reversible anion attachment/detachment, the maximum applied voltage is below that causing electrolysis of the electrolyte or water. The CV curve of the InGaN layer shows no anion-selective behavior. It shows only a displacement current of ions in the electrolyte. For the InN/InGaN QDs, the marked faradaic current peaks indicate the anion-selective behavior. The anodic and cathodic current peaks are associated with the attachment and detachment of chloride ions. Fourier-transform infrared spectroscopy reveals that there are no chemical reactions of the InN/InGaN QDs or the InGaN layer due to the high chemical stability. The InN QDs are the active sites where the dominant faradaic behavior originates.

Faradaic currents are the result of redox reactions. However, there are no chemical reactions, neither of the electrolyte or water nor of the electrode itself. There is no direct electron-charge transfer from the electrolyte to the electrode material. The origin of the faradaic currents is due to the attachment/detachment of chloride ions, releasing/capturing the same amount of electrons from/into the QDs.

Due to the take-up of ions, the InN/InGaN QD anion-selective electrode is evaluated as an electrochemical-energy storage device, more specifically as a supercapacitor electrode [39]. Supercapacitors are high-capacitance electrochemical capacitors with high power density. Batteries are characterized by high energy density. Supercapacitors complement batteries by providing fast storage or supply of large amounts of electrical energy. Most prominent examples are regenerative breaking of cars, buses, trains and electrical power-grid
stabilization. Both require storage and supply of electrical energy within seconds.

Supercapacitors are classified into electrostatic double-layer capacitors, pseudocapacitors and hybrid capacitors. The charge storage in electrostatic double-layer capacitors is in the Helmholtz double-layer at the electrode-electrolyte interface. The charge storage in pseudocapacitors, which is more efficient, is through highly reversible and fast faradaic charge-transfer processes (redox reactions, intercalation, electrosorption). In this context, the CV curve of the InGaN layer shows only capacitive currents due to electrostatic double-layer capacitance. The pronounced anodic and cathodic faradaic current peaks for the InN/InGaN QDs indicate pseudocapacitor behavior. The capacitance $C$ is evaluated from the CV curves according to:

$$C = \frac{\int I(E) dE}{\nu \Delta E},$$

where $I(E)$ is the current at electrode potential $E$, $\nu$ is the scan rate and $\Delta E$ is the electrode potential window in which the scan is performed. A high areal capacitance of 9 mF/cm$^2$ is derived for the InN/InGaN QD electrode in 1 M KCl aqueous solution at low scan rate [38]. For a planar electrode, this high areal capacitance is twice that of carbon-based materials and one order of magnitude larger than that of metal oxides [40–43].

The InN/InGaN QD electrode undergoes rapid and reversible charge/discharge cycles, measured by the galvanostatic cycling with potential limitation (GCPL) technique. Other electrolytes have also been tested. These include KBr and KF aqueous electrolytes, as well as some usual organic electrolytes such as 1 M LiClO$_4$, LiBF$_4$ and LiPF$_6$, dissolved in acetonitrile. Organic electrolytes are often used in supercapacitors to increase the energy density. They can withstand larger voltages without decomposition. The capacitance for the KBr and KF aqueous electrolytes is much smaller than that for the KCl aqueous electrolyte. The organic electrolytes show no pseudocapacitor behavior. This points to the optimum size of chloride anions for attachment to the QDs. The high affinity towards chloride ions is very interesting also in a broader sense. It opens up new solutions for water waste treatment and for the chlor-alkali industry.

**SI SUBSTRATE**

InGaN QDs have been grown on GaN [13]. InGaN layers have been grown over the entire composition range on GaN/sapphire templates [44]. InGaN layers have been grown on Si substrates, always on GaN, AlN or combined buffer layers. The growth of InN QDs on In-rich InGaN layers [45] and the growth of InGaN layers over the entire In composition range directly on Si (111) substrates without buffer layers [46] are major technological advances. It is significant because there is an ohmic contact between p-type Si and n-type In-rich InGaN (with In content around 45%). The ohmic contact is due to the alignment of the valence band of p-type Si with the conduction band of n-type InGaN. For the ohmic contact to form, the p-type Si and In-rich n-type InGaN have to be in direct contact without insulating buffer layers in between. The band alignment has been theoretically predicted [47] and now experimentally realized [46]. This allows novel device designs with simplified electrical contact schemes.

Figure 7a shows a high-resolution transmission-electron microscopy (HRTEM) image of a three-monolayer InN QD grown on an In-rich In$_{0.73}$Ga$_{0.27}$N layer on a Si (111) substrate [45]. The QD has the shape of a truncated cone; it is 4 nm high with a base width of 10 nm. Underneath the QD is a 0.9-nm thin two-dimensional InN wetting layer (WL). This is evidence of the Stranski-Krastanov growth mode. The HRTEM image of the In$_{0.73}$Ga$_{0.27}$N/Si interface region is shown in Fig. 7b [46]. Apart from occasional localized defects, the InGaN layer is compact and highly crystalline. The InGaN layer exhibits a well-defined in-plane epitaxial relation with the Si substrate. In growth direction: InGaN (0001) || Si (111). The In content varies less than 2.5% over large distances, as verified by energy-dispersive X-ray (EDX) spectroscopy.

Keys for the excellent growth behavior are (i) the low growth temperature, kinetically...
suppressing phase separation; (ii) a close to stoichiometric, slightly N-rich group V-to-III flux ratio, promoting a planar growth front; and (iii) the 2–3-nm-thick SiNx interlayer, formed by intentional nitridation of the Si surface at elevated temperature (at 850°C for five minutes) prior to growth. Though the SiNx interlayer appears amorphous, the well-defined in-plane epitaxial relation and the epitaxial relation in the growth direction of the InGaN layer with the Si substrate prove epitaxial growth. How the crystallographic information from the Si substrate is transferred is not clear. It is clear that the SiNx interlayer promotes wetting and strain relaxation of the InGaN layer at the initial stage of growth—a prerequisite for epitaxial growth.

Over the whole In composition range, the high-resolution X-ray diffraction (XRD) spectra of the InGaN layers reveal a single relatively narrow peak. This verifies the uniformity of composition and the absence of phase separation. Over the whole In composition range, the photoluminescence (PL) spectra likewise exhibit a single peak. The PL efficiency is comparable for all In contents. Distinct emission is observed up to room temperature. This is clear evidence of good optical quality. Top-to-bottom current-voltage (IV) measurements confirm the ohmic contact between the p-type Si substrate and the n-type InGaN layer for In contents around 50%.

MODEL

All three applications—the photoelectrode, the biosensor transducer and the anion-selective/pseudocapacitor electrode—have one thing in common: attraction of negative charge. For the photoelectrode and biosensor, it is oxidation, the transfer of electrons to the InN/InGaN QD electrode. For the pseudocapacitor electrode, it is the attachment of anions. This is explained by the interplay of surface and quantum properties of the QDs: the polar InN c-plane has a huge (the highest known) density of intrinsic positively charged surface donor states of $2–3 \times 10^{13}/\text{cm}^2$ [48–50] because surface states are located in the conduction band. This is an intrinsic property of the InN c-plane. It is not related to defects other than the surface itself. For InGaN compounds, the density of surface donors of the polar c-plane increases with In content, for an In content above 30–40%. Below this In content, the surface states are located in the bandgap [49]. This is similar to common semiconductors. For the perpendicular non-polar InN or InGaN m-plane, the density of surface donors is much lower. Surface donors are likely absent [50]. M-plane surface states are located in the bandgap close to the valence band maximum or below. The density of surface donors can be assumed to decrease when the surface is rotated from the c-plane to the m-plane.

The positively charged surface donors are proposed to be responsible for the attraction of negative charge or catalytic activity. This has been shown by measurements of the electrocatalytic oxidation enhancement at the surface of InGaN layers and nanostructures, which was probed with the ferro/ferricyanide redox couple. Cyclic voltammetry (CV) measurements revealed an increase of the oxidation enhancement with In content and proximity of nanostructure surfaces to the c-plane [51]. This directly correlates with the density of surface donors. Strongest enhancement is for the c-plane InGaN surface functionalized with InN QDs. First a qualitative and then a more quantitative explanation is given for this phenomenon.

For planar InGaN or InN layers, the positively charged surface donors are uniformly compensated by an electron surface accumulation layer inside the semiconductor. The Debye screening length in the electron surface accumulation layer is of the order of 1 nm for the high carrier concentration in the case of the c-plane InN surface [52]. Therefore, morphological surface features with lateral dimensions larger than $\sim 1$ nm behave like planar layers. For an InN QD with zero-dimensional, discrete electronic states, however, the Pauli-Exclusion principle forbids that enough electrons can enter the QD to uniformly screen the surface donors. The quantum repulsion dominates the screening, though the QD is larger than the screening length. This leaves an uncompensated positive net surface charge on the QD. The remaining electrons are repelled to the InGaN barrier layer underneath the QD. An electric dipole is formed. The electric dipole field actively attracts negative charge, accounting for the catalytic activity and anion selectivity. Schematically, this is presented in Fig. 8a–c.

Figure 8a shows the InN/InGaN QD photoelectrode catalysing the oxidation of water by Coulomb attraction of electrons to the QDs. Figure 8b shows the InN/InGaN QD biosensor transducer catalysing the oxidation reaction chain of glucose, again by Coulomb attraction of electrons to the QDs. Figure 8c shows the InN/InGaN QD anion-selective/pseudocapacitor electrode promoting the attachment of chloride anions by Coulomb attraction to the QDs. For each attached chloride anion, an electron is released from the QD to the bulk electrode. This process is reversible upon applying an external voltage. The anodic and cathodic faradaic currents in Fig. 6b originate from the electron transfer...
between the QDs, the artificial atoms and the bulk electrode. This is interpreted as an artificial redox reaction. No chemical reactions of the electrode or electrolyte occur.

The functionality arises from the ‘InN QDs on InGaN barrier’ combined system and not from the QDs alone. The energy barrier has to be large enough to create strong quantum confinement up to room temperature—it has to be low enough to allow sufficient electrons to be repelled from the QDs to the barrier. The energy barrier also has to be lower than the energy position of the InN surface states. Otherwise, they are neutralized. The energy position of the surface states is 0.6 eV above the conduction band minimum [50]. The present structure—InN QDs on In-rich InGaN—seems to be ideal compared to InN QDs grown on GaN [13] or directly on Si [53]. Besides, Si has only limited chemical stability.

The active Coulomb attraction of electrons or anions by the electric dipole field of the QDs makes the Nernst limit invalid. The Nernst limit concerns solely the thermodynamic equilibrium in the electrolyte. It derives from the balance of the chemical concentration gradient with the electric potential gradient. In turn, the marked transgression of the Nernst limit verifies the model of catalytic oxidation enhancement and anion selectivity by the electric dipole field of the QDs—the chloride ions taken as a probe.

For maximized efficiency, it is essential that surfaces with high catalytic activity are exposed. These are the surfaces with high surface energy. Increase of the surface area in free nanostructure growth (often only pursued) inherently leads to the exposure of low-activity planes due to minimization of the surface energy in the growth process. It is the two-dimensional epitaxial growth which makes possible the exposure of surfaces with high catalytic activity/surface energy. The exposure is imprinted by the epitaxial relation with the substrate. This is a new aspect of two-dimensional epitaxial growth. For freely formed nanostructures, high-activity planes may be exposed by heating to high temperatures. This is not practical and often not applicable.

In the case of photoelectrochemical water splitting and also amperometric sensing, the situation is somewhat more complex. The overall efficiency/sensitivity depends not only on the catalytic activity of the surface, but also on the light absorption due to surface texture and surface area. In general, the optimum balance between catalytic activity of different planes and surface morphology/surface area needs to be found.

The high density of intrinsic positively charged surface donors has another aspect of equal importance. It protects the electrode surface against corrosion—most critically photocorrosion in the case of photoelectrochemical water splitting [54]. The surface donors have transferred an electron to the underlying semiconductor. This protects the surface against further donation of electrons or acceptance of holes, which is oxidation/corrosion. In other words, the positively charged surface donors and corresponding electron surface accumulation layer are described by a steep downward energy-band bending near the surface. This pushes the semiconductor oxidation potential down in energy, unreachable for holes to oxidize the surface. The holes rather tunnel into the solution to efficiently oxidize the target. A scheme of the energy-band diagram is drawn in Fig. 8a. It includes the charge-carrier transfer for the case of photoelectrochemical water splitting and the Fermi energy for degenerate InGaN with donor-like defects.

In general, protection of the surface against corrosion and the catalytic oxidation enhancement have the same origin which is amplified by the QDs through the additional charge separation. Common

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**Figure 8.** Scheme of the (a) InN/InGaN QDs catalysing the oxidation of water, (b) InN/InGaN QDs catalysing the oxidation reaction chain of glucose and (c) InN/InGaN QDs attracting Cl$^{-}$ ions.
n-type semiconductors and also m-plane InN exhibit electron depletion near the surface. Surface states are located in the bandgap or below. The near-surface energy-band bending is upwards. This promotes corrosion and hinders oxidation of the target.

To be more quantitative, the InN QD shown in the HRTEM image in Fig. 7a is considered. The QD has a height of 4 nm and a base width of 10 nm. For an assumed circular shape of the QD and a density of positively charged surface donors of $2 \times 10^{13}$ cm$^{-2}$, 16 donors are situated on the QD top surface (approximated by a circular disk). The QD sidewalls are not considered. For others than the c-plane, the surface donor density is not known quantitatively. Certainly, the surface donor density of the sidewalls is lower than that of the c-plane. The QD sidewalls are tilted towards the m-planes with the lowest or zero density of surface donors [50]. This justifies neglecting the QD sidewalls in a first approximation.

The number of bound states of a QD of that size is limited, likely to four [55], accommodating eight electrons. This estimate is reasoned, since the energetics of the InN/InGaN QDs [11,45] is basically the same as that of InAs/GaAs QDs [55]. Hence, eight surface donors are uncompensated and the remaining eight electrons are quantum mechanically repelled to the InGaN barrier layer underneath the QD. The resulting charge distribution is approximated by two oppositely charged circular disks. Each disk accommodates eight elementary charges. The radius of the disks is $R = 5$ nm and their distance (QD height) is $h = 4$ nm. The electric potential $V(x)$ of a single charged circular disk at a distance $x$ on the axis of the disk is

$$V(x) = 2\pi \sigma \frac{1}{4\pi \varepsilon_0 \varepsilon_r} \left[ \frac{1}{\sqrt{x^2 + R^2}} - \frac{1}{|x|} \right].$$

(4)

Then, the potential difference $V$ in the center of the two oppositely charged disks with distance $h$ is

$$V = V(x=0) - V(x=h) = 2\pi \sigma \frac{1}{4\pi \varepsilon_0 \varepsilon_r} \left[ R + h - \sqrt{h^2 + R^2} \right],$$

(5)

where $\varepsilon_0$ is the vacuum permittivity, $\varepsilon_r$ is the relative permittivity of InN and $\sigma$ is the uncompensated surface donor charge density or repelled electron-charge density. For the catalytic efficiency and anion selectivity, it is this potential difference which is relevant. It stands for the reduction of the overpotential for an electrochemical reaction or the energy gain when anions are attached. The potential difference amounts to 180 mV. This value is well in the range to account for the experimental results. Though very simple, the model further provides a guide to maximize the catalytic efficiency or anion selectivity by tuning the QD size, shape and density for maximized potential difference. Even the charge distribution might be matched to a certain electrochemical reaction or ion shape for maximized catalytic activity and anion attachment.

**CONCLUSIONS**

The exceptional performance of epitaxial InN/InGaN QDs as electrode material for electrochemical devices was reviewed and brought in relation to the performance of other reported materials. First, the three most relevant device applications were discussed: (i) photoelectrodes for photoelectrochemical hydrogen generation by water splitting for solar-energy harvesting and storage; (ii) enzymatic biosensors for the detection of glucose and cholesterol for medical diagnostics; and (iii) anion-selective electrodes for the detection of chloride ions, which were also evaluated as supercapacitor electrodes. The 6% solar-to-hydrogen efficiency at zero external voltage, rising to above 15% for 0.4-V external voltage, and the sensor sensitivities above 90 mV/decade are unmatched. Then, the epitaxial growth of InN/InGaN QDs and InGaN layers over the entire In composition range directly on cheap Si substrates without any buffer layers was demonstrated, enabling minimized cost, novel device designs and integration with Si technology. Finally, a model for the superior electrochemical performance of the InN/InGaN QDs based on the unique surface and quantum properties was put forward. The model provided a semi-quantitative understanding of the boost of catalytic activity, anion selectivity and corrosion resistance. This link of quantum nanostructure physics with electrochemistry and catalysis provides new directions for future research and new application fields. Researching epitaxial quantum nanostructures for electrochemical devices in the same spirit as is done for optical and electrical devices will make them equally successful in this wide, so far unexplored area.

**ACKNOWLEDGEMENTS**

The author gives thanks for fruitful collaboration and discussions with N.H. Alvi, P.E.D. Soto Rodríguez, P. Kumar, P. Aseev, V.J. Gómez, Technical University of Madrid, Spain; A.H. Alvi, University of Agriculture, Faisalabad, Pakistan; W. Hassan, Bahauddin Zakariya University, Multan, Pakistan; S. Zaman, G. Amin, O. Nur, M. Willander, Linköping University, Sweden; J.M. Manuel, F.M. Morales, J.J. Jiménez, R. García, University of Cádiz, Spain; A. Senichev, Max Planck Institute of Microstructure Physics,
Halle, Germany; C. Lienau, Carl von Ossietzky Universität, Oldenburg, Germany; C.M. Mari, S. Sanguinetti, R. Ruffo, University Milano Bicocca, Italy.

Conflict of interest statement. None declared.

REFERENCES

1. Lu YS, Huang CC and Yeh JA et al. InN-based anion selective sensors in aqueous solutions. Appl Phys Lett 2007; 91: 202109.
2. Waki i, Cohen D and Lal R et al. Direct water photoelectrolysis with patterned n-GaN. Appl Phys Lett 2007; 91: 093519.
3. Lu YS, Ho CL and Yeh JA et al. Anion detection using ultrathin InN ion selective field effect transistors. Appl Phys Lett 2008; 92: 212102.
4. Chaniotakis N and Sofikiti N. Novel semiconductor materials for the development of chemical sensors and biosensors: a review. Anal Chim Acta 2008; 615: 1–9.
5. Li J, Lin JY and Jiang HX. Direct hydrogen gas generation by using InGaN epitaxial layers as working electrodes. Appl Phys Lett 2008; 93: 162107.
6. Hwang YJ, Wu CH and Hahn C et al. Si/InGaN core/shell hierarchical nanowire arrays and their photoelectrochemical properties. Nano Lett 2012; 12: 1678–82.
7. Al Otaibi B, Harati M and Fan S et al. High efficiency photoelectrochemical water splitting and hydrogen generation using GaN nanowire photoelectrode. Nanotechnology 2013; 24: 175401.
8. Benton J, Bai J and Wang T. Enhancement in solar hydrogen generation efficiency using a GaN-based nanorod structure. Appl Phys Lett 2013; 102: 173905.
9. Benton J, Bai J and Wang T. Utilisation of GaN and InGaN/GaN with nanoporous structures for water splitting. Appl Phys Lett 2014; 105: 223902.
10. Kibria MG, Chowdhury FA and Zhao S et al. Visible light-driven efficient overall water splitting using p-type metal-nitride nanowire arrays. Nat Commun 2015; 6: 6797.
11. Soto Rodriguez PED, Gómez VJ and Kumar P et al. Near-infrared InN quantum dots on high-In composition InGaN. Appl Phys Lett 2013; 102: 131909.
12. Liu AY, Srinivasan S and Norman J et al. Quantum dot lasers for silicon photonics. Photonics Res 2015; 3: B1–9.
13. Grandjean N and Ilegems M. Visible InGaN/GaN quantum-dot materials and devices. Proc IEEE 2007; 95: 1853–65.
14. Luque A, Martí A and Stanley C. Understanding intermediate-band solar cells. Nat Photonics 2012; 6: 146–52.
15. Osterloh FE and Parkinson BA. Recent developments in solar water-splitting photocatalysis. MRS Bull 2011; 36: 17–22.
16. Cho S, Jiang JW and Lee KH et al. Research update: strategies for efficient photoelectrochemical water splitting using metal oxide photoanodes. APL Mat 2014; 2: 010703.
17. May MM, Lewerenz HJ and Lackner D et al. Efficient direct solar-to-hydrogen conversion by in situ interface transformation of a tandem structure. Nat Commun 2015; 6: 8286.
18. Kim TW and Choi KS. Nanoporous BiVO4 photoanodes with dual-layer oxygen evolution catalysts for solar water splitting. Science 2014; 343: 990–4.
19. Khaselev O and Tumer JA. A monolithic photovoltaic-photoelectrochemical device for hydrogen production via water splitting. Science 1998; 280: 425–7.
20. Moses PG and Van de Walle CG. Band bowing and band alignment in InGaN alloys. Appl Phys Lett 2010; 96: 201908.
21. Alvi NH, Soto Rodriguez PED and Aseev P et al. InN/InGaN quantum dot photoelectrode: efficient hydrogen generation by water splitting at zero voltage. Nano Energy 2015; 13: 291–7.
22. Yang X, Liu R and Ho Y et al. Enabling practical electrocatalyst-assisted photoelectrochemical water splitting with earth abundant materials. Nano Research 2015; 8: 56–81.
23. Holzinger M, Le Goff A and Cosnier S. Nanomaterials for biosensing applications: a review. Front Chem 2014; 2: 1–10.
24. Medintz IL, Uyeda HT and Goldman ER et al. Quantum dot bioconjugates for imaging, labelling and sensing. Nat Mater 2005; 4: 435–46.
25. Frasco FM and Chaniotakis N. Semiconductor quantum dots in chemical sensors and biosensors. Sensors 2009; 9: 7266–86.
26. Algar WR, Tavares AJ and Krull UJ. Beyond labels: a review of the application of quantum dots as integrated components of assays, bioprobes, and biosensors utilizing optical transduction. Anal Chim Acta 2010; 673: 1–25.
27. Alvi NH, Soto Rodriguez PED and Gómez VJ et al. Highly efficient potentiometric glucose biosensor based on functionalized InN quantum dots. Appl Phys Lett 2012; 101: 153110.
28. Alvi NH, Soto Rodriguez PED and Gómez VJ et al. An InN/InGaN quantum dot electrochemical biosensor for clinical diagnosis. Sensors 2013; 13: 13917–27.
29. Israr MQ, Sadaf JR and Nur O et al. Chemically fashioned ZnO nanowalls and their potential application for potentiometric cholesterol biosensor. Appl Phys. Lett. 2011; 98: 253705.
30. Israr MQ, Sadaf JR and Asif MH et al. Potentiometric cholesterol biosensor based on ZnO nanorods chemically grown on Ag wire. Thin Solid Films 2010; 519: 1106–9.
31. Dimeski G, Badrick T and John AS. Ion selective electrodes (ISEs) and interferences: a review. Clin Chim Acta 2010; 411: 309–17.
32. Claudio Zuliani C and Diamond D. Opportunities and challenges of using ion-selective electrodes in environmental monitoring and wearable sensors. Electrochem Acta 2012; 84: 29–34.
33. Huang MR, Ding YB and Li XG. Ion selective electrodes based on sensing membrane without or with reduced amounts of plasticizer. Acta Phys Chim Sin 2013; 29: 1–10.
34. Amemiya S, Kim J and Izadyar A et al. Electrochemical sensing and imaging based on ion transfer at liquid/liquid interfaces. Electrochem Acta 2013; 110: 836–45.
35. Yanab R, Quaa S and Tonga L et al. Review of progresses on clinical applications of ion selective electrodes for electrolytic ion tests: from conventional ISEs to graphene-based ISEs. Chem Spec Bioavailab 2016; 28: 72–7.
36. Tminka L, Adam V and Hubalek J et al. Amperometric sensor for detection of chloride ions. Sensors 2008; 8: 5619–36.
37. Alvi NH, Soto Rodriguez PED and Gómez VJ et al. Highly sensitive and fast anion selective InN quantum dot electrochemical sensors. Appl Phys Express 2013; 6: 115201.
38. Soto Rodriguez PED, Mari CM and Sanguinetti S et al. Epitaxial InN/InGaN quantum dots on Si: Cl⁻ anion selectivity and pseudocapacitor behavior. Appl Phys Express 2016; 9: 081004.
39. Conway BE. Transition from ‘supercapacitor’ to ‘battery’ behavior in electrochemical energy storage. J Electrochem Soc 1991; 138: 1539–48.
40. Burke A. Ultracapacitors: why, how, and where is the technology. J Power Sources 2000; 91: 37–50.
41. Simon P and Gogotsi Y. Materials for electrochemical capacitors. Nat Mat 2008; 7: 845–54.
42. Obreja VVN. Supercapacitors specialities—materials review. AIP Conf Proc 2014; 120: 98–120.
43. Chen SM, Ramachandran R and Mani V et al. Recent advancements in electrode materials for the high-performance electrochemical supercapacitors: a review. Int J Electrochem Sci 2014; 9: 4072–85.
44. Ilipoulos E, Georgakilas A and Dimakis E et al. InGaN(0001) alloys grown in the entire composition range by plasma assisted molecular beam epitaxy. Phys Stat Sol (a) 2006; 203: 102–5.
45. Soto Rodriguez PED, Aseev P and Gómez VJ et al. Stranski-Krastanov InN/InGaN quantum dots grown directly on Si (111). Appl Phys Lett 2015; 106: 023105.
46. Aseev P, Soto Rodriguez PED and Gómez VJ et al. Near-infrared emitting In-rich InGaN layers grown directly on Si: towards the whole composition range. Appl Phys Lett 2015; 106: 072102.
47. Hsu L and Walukiewicz WJ. Modeling of InGaN/Si tandem solar cells. J Appl Phys 2008; 104: 024507.
48. Mahboob I, Veal TD and McConville CF et al. Intrinsic electron accumulation at clean InN surfaces. Phys Rev Lett 2004; 92: 036804.
49. Veal TD, Jefferson PH and Piper LFJ et al. Transition from electron accumulation to depletion at InGaN surfaces. Appl Phys Lett 2006; 89: 202110.
50. Van de Walle CG and Segev D. Microscopic origins of surface states on nitride surfaces. J Appl Phys 2007; 101: 081704.
51. Soto Rodriguez PED, Calderon Nash V and Aseev P et al. Electrocatalytic oxidation enhancement at the surface of InGaN films and nanostructures grown directly on Si (111). Electrochim Commun 2015; 60: 158–62.
52. Laubsch A, Urban K and Ebert P. Three- to two-dimensional transition in electrostatic screening of point charges at semiconductor surfaces studied by scanning tunneling microscopy. Phys Rev B 2009; 80: 245314.
53. Kumar M, Roul B and Shetty A et al. Temperature dependent transport studies in InN quantum dots grown by droplet epitaxy on silicon nitride/Si substrate. Appl Phys Lett 2011; 99: 153114.
54. Chen S and Wang LW. Thermodynamic oxidation and reduction potentials of photocatalytic semiconductors in aqueous solution. Chem Mater 2012; 24: 3659–66.
55. Wang LW, Kim J and Zunger A. Electronic structure of [110]-faceted self-assembled pyramidal InAs/GaAs quantum dots. Phys Rev B 1999; 59: 5678–87.