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InN/InGaN Quantum Dots: A Surprise for Highly Sensitive and Fast Potentiometric Biosensors

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The development of highly sensitive and fast biosensors with good reproducibility and specificity is the main focus of the biosensing research community because it offers a great opportunity for the diagnosis of many major life threatening diseases and their treatments at early stages. Therefore, the health industry urgently needs the development of more efficient, reliable, and cheap sensing and detection technologies. Towards this goal we demonstrate epitaxially grown InN quantum dots (QDs) for fast, highly sensitive, and efficient potentiometric biosensors owing to their low-dimensionality and unique electronic properties.

The InN QDs are grown by plasma-assisted molecular beam epitaxy (PA-MBE) on a 80 nm thick high-In-composition $In_{0.54}Ga_{0.46}N$ layer on a (0001) GaN/sapphire substrate. They are bio-chemically functionalized for the detection of glucose and cholesterol molecules. The such fabricated InN QDs based biosensor exhibits excellent linear electrochemical response with high sensitivity of 80 and 96 mV/decade for glucose and cholesterol molecules over a wide logarithmic glucose and cholesterol concentration range. The InN QDs based biosensor also reveals fast response time of less than 2 seconds with good stability and reusability and shows negligible response to common interferents such as ascorbic acid and uric acid. The InN QDs based biosensors, hence, has full potential to be an attractive candidate for clinical diagnoses and has the potential to replace and compete with other available diagnostic devices. The InN QDs are compared with InN thin films, also grown on a 80 nm thick $In_{0.54}Ga_{0.46}N$ layer, having the same surface properties but different morphology and electronic properties. The sensitivity of the InN QDs based biosensor is twice that of the InN thin film based biosensor, the EMF is three times larger, and the response time is five times shorter. This reveals that the superior biosensing properties of the InN QDs are related to their zero-dimensional nature and not only to the surface properties.

InN nanostructures especially QDs are becoming very attractive candidates for biosensing applications due to their low-dimensionality and unique electronic properties [1].InN nanostructures contain positively charged surface donor states with a density as high as 10^{13} cm^{-2} which causes the highest native electron accumulation observed in III-V semiconductor nanostructures [2-4]. Due to this high surface charge density and robust surface properties, InN nanostructures have been proposed to be useful for sensing applications [5-6].

The development of biosensors based on InN QDs is potentially very interesting taking advantage of their zero-dimensional electronic properties together with the high density of positively charged surface donor states. For a density of positively charged surface donor states of the order of 10^{13} cm^{-2}, about 40-70 donors are situated on the QDs when taking into account the QD diameter of 20 – 30 nm. Due to the zero-dimensional quantum confinement of carriers, however, the QDs each can accommodate only two electrons in the ground state. Even when considering the presence of excited states, this results in a local net positive charge of the QDs with the compensating electrons expelled to their surroundings. This positive net charge actively promotes the oxidation of glucose and cholesterol, i.e., the transfer of electrons to the QDs working electrode, setting the electrochemical potential with respect to the reference electrode. Notably, the experimental results show, that this can lead to a sensitivity which is beyond the Nernst limit of 59 mV/decade. For the InN thin film, on the other hand, the positively charged surface donors are uniformly compensated by the accumulated electrons in the semiconductor and no specific sites promoting the oxidation of glucose or cholesterol are present. Fig. 1 (a-c) shows the atomic force microscopy (AFM) images of the InN QDs, InN thin film, and bare InGaN layer, respectively. The QDs exhibit a height of 2-3 nm, diameter of 20-30 nm, and density of 2.2×10^{9} cm^{-2}.

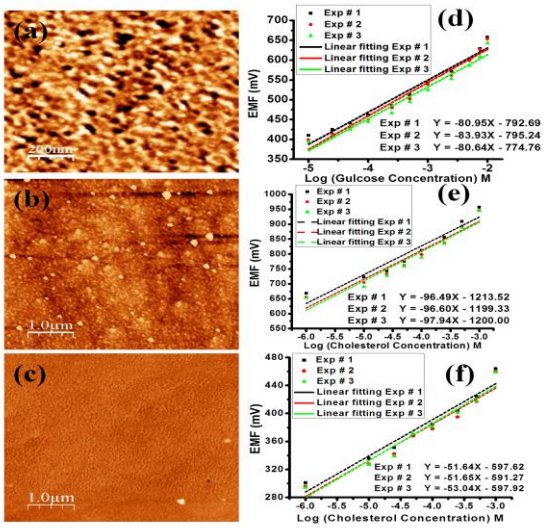

Fig. 1 (a-c) AFM images of the InN QDs, InN thin film, and InGaN layer. (d,e) EMF as a function of the logarithmic glucose and cholesterol for the InN thin film. Exp # 1 – 3 denote three different experiments.

Figure 1 (d,e) shows the EMF response of the InN QDs based biosensor measured for different glucose and cholesterol concentrations. The EMF is linear versus the logarithmic nutrients concentrations and shows a significantly high slope of 80 and 96 mV/decade, respectively. Figure 1 (d,e) shows the EMF response of the InN QDs based biosensor measured for concentrations for the InN QDs. (f) EMF as a function of the logarithmic cholesterol concentration Figure 1 (f) shows the EMF response of the InN thin film based biosensor for different cholesterol concentrations. The EMF is linear versus the logarithmic concentration and shows a slope of 51 mV/decade. Repeated experiments (denoted Exp # 1 - 3) with the same biosensors show reproducible results confirming the stability, linearity, and reusability of the biosensors.

Figure 2 (a,b) shows the EMF response as a function of time of the InN QDs based biosensor for glucose and cholesterol detection while Fig. 2 (c) shows that of the InN thin film based biosensor for cholesterol detection. The biosensor based on the InN QDs delivers a 5 times faster EMF response in comparison with the biosensor based on the InN thin film. The output signal of the InN QDs based biosensor is stable within 0.5% after two seconds, while it takes about 10 seconds for the InN thin film based biosensor. The time response for the bare InGaN layer, which was also measured for glucose detection, is much slower and the maximum EMF is significantly lower. The EMF is not stable and drops in time, as shown in Fig. 2 (d). This confirms the major contribution of

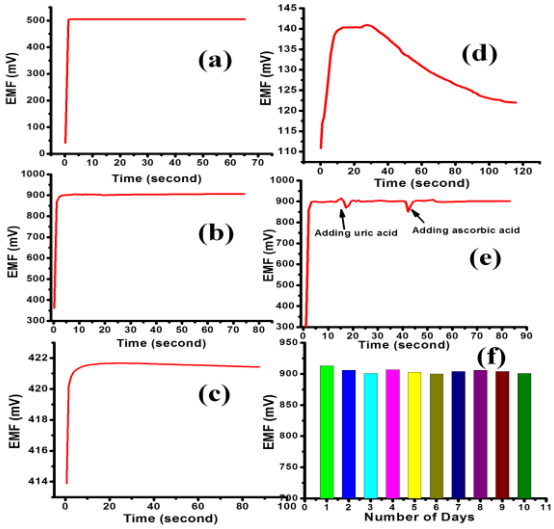

Fig. 2 EMF as a function of time (a,b) for the InN QDs for glucose and cholesterol detection, (c) for the (e) EMF as a function of time for the InN QDs when adding ascorbic acid or uric acid to the glucose solution. (f) EMF for the InN QDs measured for ten consecutive days using same biosensor.

the InN QDs. The selectivity of the InN QDs based biosensor was also investigated, in particular with regard to well-known interfering agents such as ascorbic acid and uric acid. Upon the addition of ascorbic acid or uric acid to the cholesterol solution the EMF does not substantially change as shown in Fig. 2 (e).This reveals the good selectivity of the biosensor. Moreover, the InN QDs based biosensor exhibits excellent storage stability as evidenced by a series of repeated experiments for ten consecutive days as shown in Fig. 2 (f). These measurements were performed to ensure that the biosensor retains its sensitivity and reusability for long durations of time needed for routine clinical diagnoses applications.

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