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Three-Dimensional Nanostructured Cadmium Selenide Multi-Pods Directly Grown on Substrate by Microwave-Assisted Chemical Synthesis and Their Application as Photo-Switches for Label-Free DNA Sensing

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Abstract

Nanostructured Cadmium Selenide Multi-Pods (CdSe MPs) grown directly on a conducting substrate are reported. The resultant CdSe MP electrode shows differentiable photo-response towards blue light illumination upon surface attachment of single-stranded and double-stranded DNA molecules. A simple photoswitching "ON/OFF" test can be designed and implemented to recognize hybridized product of probe DNA molecules and its fully complementary target counter-part.

Introduction

Cadmium Selenide (CdSe) is an important II-VI semiconductor. It has a direct band gap of 1.74 eV at 300 K, which lies within the visible spectrum. Therefore, it has been a subject of intensive study in photonic applications [1-3]. Bulk CdSe has been extensively investigated in the last decades due to its application in photovoltaic cells, thin film transistors, optical-data recording and other optoelectronic devices [4]. With the increasing attention and knowledge on synthesis of nanostructured CdSe (0D and 1D), focus has been put on its new and potential applications such as biosensors, in particular DNA sensing due to its extraordinary optoelectronic properties with quantum confinement effect, high surface to volume ratio and thus much higher sensitivity towards surface modifications. For example, our previous study has demonstrated the use of CdSe quantum dot monolayer for DNA sensing [5]. Here, we reported a novel preparation of three-dimensional (3D) nanostructured CdSe Multi-Pods (MPs) directly grown on substrate by microwave-assisted chemical synthesis. The Indium-Tin-Oxide (ITO) substrate so coated with CdSe MPs demonstrated enormous potential as photo-switches for label-free DNA sensing. Rapid, label-free, and portable DNA sensing devices are one of the mostly sought-after bio-devices for applications in bio-threat detection and point-of-care diagnostics [6-8]. A high-performance device should exhibit high sensitivity and selectivity, together with portability and robustness. Also, simple operation and fast readout are always preferred. The developed label-free DNA sensing platform bears the potential to be such a high-performance device which is very attractive practical use.

Results and Discussion

ITO/glass substrates (1 × 1 cm^2) were cleaned with Decon® detergent to remove any organic impurities. The substrates were then treated with oxygen plasma for 1 minute to achieve a clean surface for subsequent processes. In order to improve the adhesion of CdSe MPs on substrates, the cleaned ITO substrates were firstly electrodeposited with an ultra-thin CdSe coating (~20 nm) by using an electrochemical workstation (CHI 660C, CH Instrument Company) in an electrolyte of 0.1 M $CdCl_2$, 0.3 mM SeO_2 and 0.5 M HCl as reported by Kressin, et al. [9]. In a three-electrode electrochemical setup (working electrode: ITO/glass; counter electrode: platinum mesh; reference: saturated silver/silver chloride electrode), ultra-thin CdSe coating was achieved through cyclic depositions of 200 sweeps from -0.35 V to -0.75 V at a sweep rate 0.05 V/sec. Coated ITO/glass substrates were then rinsed with deionized water. Microwave-assisted chemical synthesis of CdSe MPs was performed with a microwave synthesizer (Discover S-Class, CEM Corporation, USA). The chemical recipe included cadmium acetate dihydrate ($(CH_3COO)_2Cd \cdot 2H_2O$), selenium (Se) powder (100 mesh) and ethylenediamine ($C_2H_8N_2$, EDA) purchased from Sigma-Aldrich and they were used as-purchased without further purification. Each ITO/glass coated with an ultra-thin CdSe layer was placed into a 35mL sealed vessel containing

0.0533 g $(CH_3COO)_2Cd \cdot 2H_2O$ and 0.0079 g Se powder in 4 mL of EDA. The reaction mixture was held for 3 minutes at a target temperature of 145˚C with a microwave power of 250 W and under a pressure of 54 psi with intensive stirring. After reaction, the vessel was taken out and let cool to the room temperature. Then, the sample was collected, rinsed with ethanol and left dry. The dried ITO/glass electrode coated with CdSe MPs was kept in a lightproof container under vacuum to avoid the degradation of the electrode before further use. Figure 1 (a) and (b) show the scanning electron micrographs of CdSe MPs grown on an ITO/glass substrate using microwave-assisted chemical synthesis.

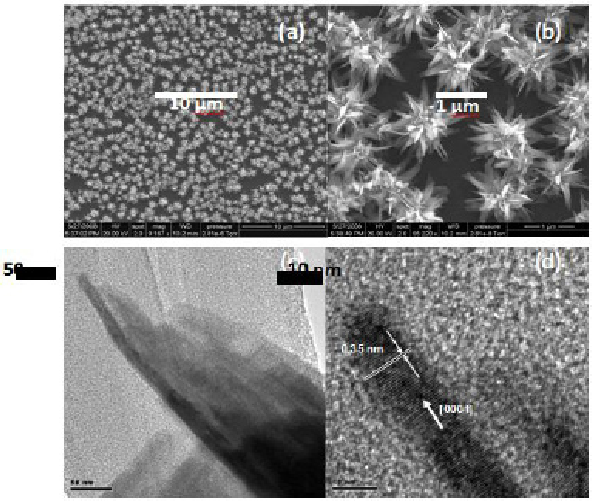

Figure 1(a-d): (a) and (b) Scanning electron micrographs of CdSe MPs directly grown on substrate by microwave-assisted chemical synthesis at different magnifications. (c) Transmission electron micrograph of a section of CdSe MP. (d) High resolution transmission electron micrograph of a section of a tip end of CdSe MP.

As shown, urchin-like CdSe MPs were found grown uniformly over the ITO/glass substrate. The MPs are all in approximately the same size of 1 µm in diameter, with spikes of nanoscale outstretching to all directions. X-ray diffraction analysis (Figure 2) confirms the hexagonal structure of the CdSe formed (JCPDS Card No. 020330). High resolution transmission electron microscopy was performed on CdSe MPs scratched off from the sample and collected by a lacey-carbon coated copper grid. Figure 1(c) shows a section of a CdSe MP particle, and Figure 1(d) shows a high-resolution transmission electron microscopic image on a tip end of a MP. It clearly shows the mono-crystallinity of each spike and the growth of CdSe is along the [0001] direction of a hexagonal CdSe crystal structure.

With the CdSe MP electrode ready, DNA molecules in single-stranded (ssDNA) or double-stranded (dsDNA) form were attached onto the bare CdSe MP electrode. It was done by immersing the CdSe MP electrode into a solution of DNA molecules at a concentration of 100 µM in a Phosphate Buffered Saline (PBS) solution for overnight. Under this treatment, the phosphate groups of the DNA backbone can interact with the surface of CdSe nanocrystals as surface capping molecules similar to trioctylphosphine oxide on CdSe nanoparticles as many reported [10]. This results in having the DNA molecules lying onto the CdSe MP surface as shown in Figure 3.

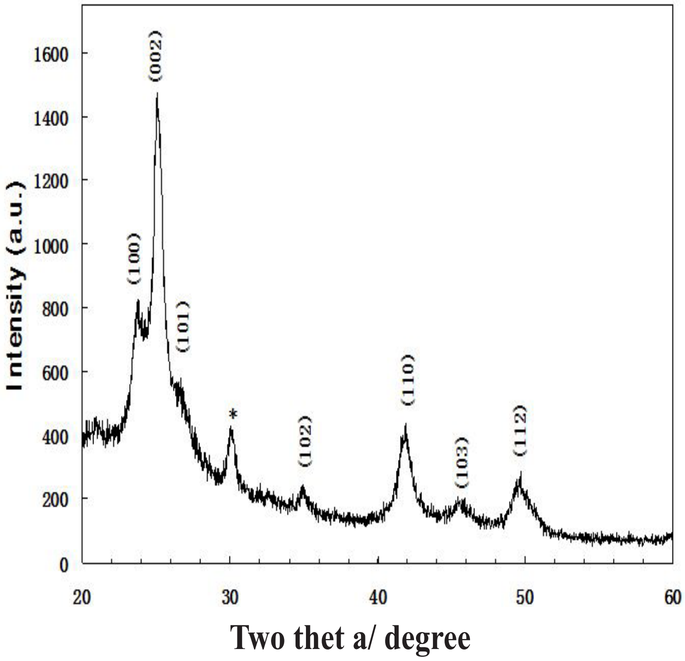

Figure 2: X-ray diffractogram of CdSe MP on substrate. The peak denoted with an asterisk originated from the ITO substrate.

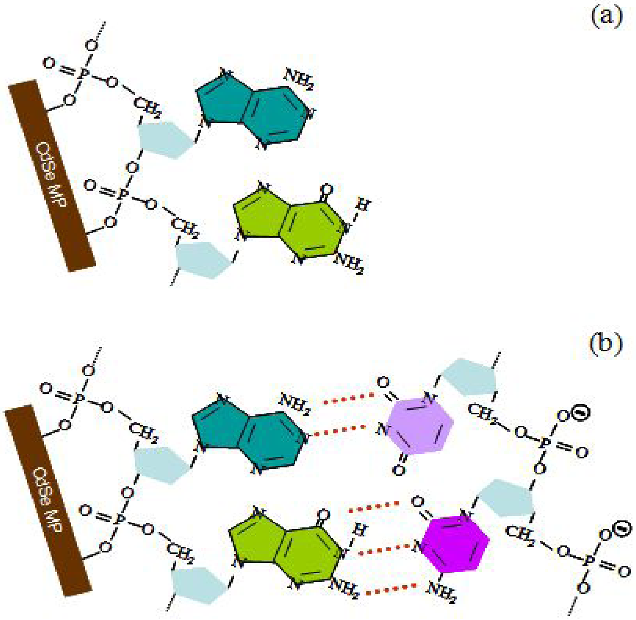

Figure 3: Diagrams showing parts of the CdSe MP surfaces attached with (a) a ssDNA molecule, and (b) a dsDNA molecule.

The DNA (ssDNA or dsDNA) attached CdSe MP electrode was then connected as the working electrode in a CHI 660C electrochemical workstation, and dipped into an aqueous solution of iodine/iodide (I_3^-/I^-, 0.2 mM I_2, 2 mM LiI) against a Pt-wire as a counter electrode at a fixed separation. The ssDNA is a 20-base DNA oligomer with a randomly selected sequence; while dsDNA is the hybridized product of this 20-base DNA oligomer with its complementary DNA oligomer. The whole setup was kept in a Faraday cage and the connections were specifically designed to reduce background electrical noises, which allowed current measurement down to tens of pico-Ampere. At a constant potential of -0.2 V applied to the CdSe MP electrode, the current variation was recorded under a manually controlled intermittent light illumination from a blue LED (LUXEON K2 (455 nm), 435 mW, Philips). Figure 4 shows two representative results of these photo-switching “ON/OFF” tests.

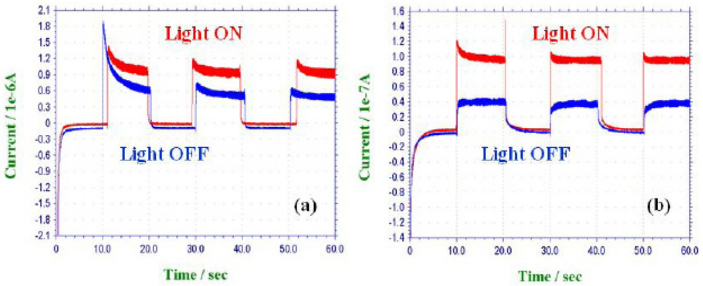

Figure 4: “ON/OFF” tests on CdSe MP electrode surface attached with (a) ssDNA and (b) dsDNA in I3-/I- electrolyte.

Generally, for the CdSe MP electrode surface attached with ssDNA molecules, the photocurrent dropped to 65-70% of the amount exhibited by bare CdSe MP electrode before attachment; while the drop was down to 40% after dsDNA surface attachment. The photo-response of CdSe MP electrodes with ssDNA and dsDNA surface attachment can be clearly differentiated. Upon light illumination, the DNA overlayer can impose a blocking effect to interaction between CdSe MP and electrolyte. A lowering of photocurrent would be expected after DNA attachment. Furthermore, between ssDNA/CdSe MP and dsDNA/CdSe MP electrodes, the later one bears additional negative surface charges provided by the free phosphate groups as illustrated in Figure 3(b). As such, during the cathodic scan that was the regime of interest, the layer of negative surface charges on CdSe MP electrode surface attached with dsDNA molecules would repel the incoming I3- for reduction. Also, they provide a counter-potential in opposite to the forward biasing. Both effects render an even more weakened photo-response in terms of photocurrent. Beside photo-response in term of photocurrent, a closer look to the profiles (Figure 4) reveals a clear difference in the transient response towards the ON/OFF of light illumination: ssDNA/CdSe MP electrode showed a much sharper and faster response than dsDNA/CdSe MP electrode, which is expected to be strongly associated with the exciton lifetime affected by the surface DNA attachment. This phenomenon is being further investigated by transient spectroscopy for deeper understanding to the corresponding electronic and opto-electronic processes across the DNA-attached CdSe surface.

Conclusion

The present work presented a facile way to prepare 3D nanostructured CdSe MPs directly grown on substrate. The subsequent CdSe MP electrode formed was demonstrated to give differentiable photo-response upon surface attachment of ssDNA and dsDNA molecules. The present work gives evidence and rationale of applying 3D nanostructured CdSe electrode for DNA sensing, while systematic study over the photo-response of the reported CdSe MP electrode towards attachment of hybridized products of DNA sequences with mismatched base pair(s) is under progress that involves investigations over a large parametric space including number and location of mismatched points, configuration of DNA molecules, and etc., thus arousing awareness over its potential in more complicated DNA recognition. Furthermore, this CdSe MP electrode can find potential applications in other opto-electronic devices, for examples as the mesoscopic TiO_2 electrode in the well-known “Grätzel Cell” [11].

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