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Functionalization of a Single TiO_2 Nanotube for Bio Sensor Applications

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Interests in one-dimensional structures as a material for emerging applications in chemical and bio sensors increase due to their unique physical properties, which arises from their dimensionality and size effects [1]. Single TiO_2 nanotubes can be employed as biochemical detectors because they are nontoxic and provide not only a large surface area to volume ratio, but also an open capped structure. Even though the TiO_2 nanotubular structure is suitable for sensor applications, it is necessary to improve their selectivity and detection limit in order to identify certain chemical and biological species. In this research, we discuss the effects of functionalizing stand-alone TiO_2 nanotube devices in order to enhance their sensing capabilities.

TiO_2 nanotubes with various wall thickness (10~40 nm) were fabricated using the combined atomic layer deposition (ALD) and nano-template method. To fabricate a test device, single TiO_2 nanotubes were dispersed on Au/Cr electrodes patterned on a Si/SiO_2 substrate and were connected to the electrode by a focused ion beam (FIB) litho technique as shown in figure 1 (a). Single TiO_2 nanotubes exhibited N-type semiconductor characteristics due to oxygen vacancies found in their structures. The conductance of the nanotube is modulated by depletion and accumulation of local charge status, such as H_2O molecules on the nanotube's surface which cause depletion of the nanotube as shown in figure 1 (b). Sensing signal-to-noise ratio, that is a sensitivity of the nanotube device, relies on the ratio between depletion width and the conductive region where is determined by the doping level (concentration of oxygen defects), number of absorbed species on the surface (localized charge), and wall thickness.

As illustrated in figure 2(a), the surface of the nanotube was immobilized by a biotin solution. The single TiO_2 nanotube device is immersed in a biotin ethanol based solution (6 mmol/L) for 3 hours. Absorbed biotin is saturated after the immersion as shown in figure 2 (b). When biotin is adsorbed on the surface of the nanotube at an oxygen vacancy site ($V_{\ddot{O}}$), N-type TiO_2 nanotubes become depleted as shown in figure 2 (c). This device was employed to detect streptavidin which is a tetrameric protein purified from bacterium. The biotin and straptavidin have a strong non-covalent bond between them, an example of how a nanotube can serve as a biosensor [2]. The devices were immersed into the streptavidin solution which was ethanol based 10 mmol/L for 1 hour. The electrical conductance change, as shown in figure 2 (c), is based upon the amount of binding of streptavidin to the surface of the TiO_2 nanotube. It can be explained that the streptavidin which is negatively charged will deplete the nanotube, which acts like a semiconductor. The mechanism by which TiO_2 nanotubes detect streptavidn can be altered to detect other bio-molecules such as antibodies and virus shell proteins for early detection of diseases.

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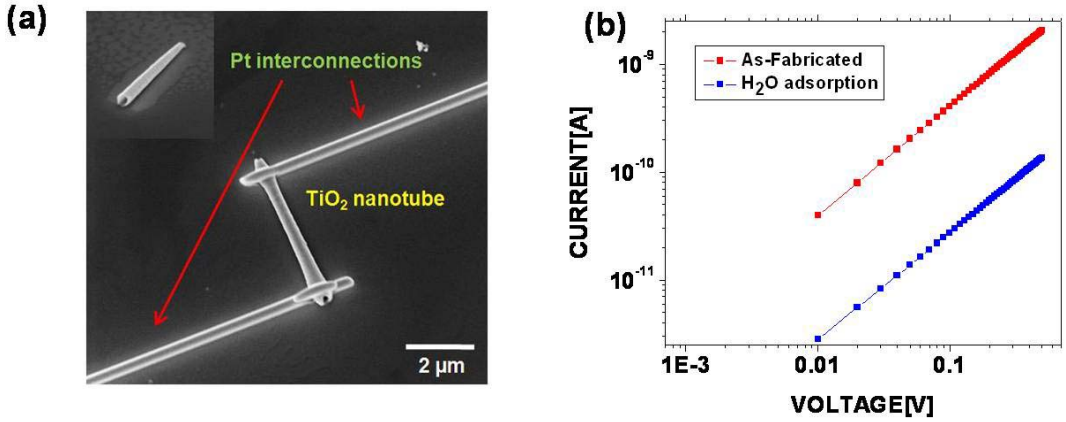

Figure 1. (a) FE-SEM micrographs showing a single stand-alone TiO_2 nanotube device fabricated by FIB and (b) I-V characteristics of the device as fabricated and after H_2O adsorption (depletion).

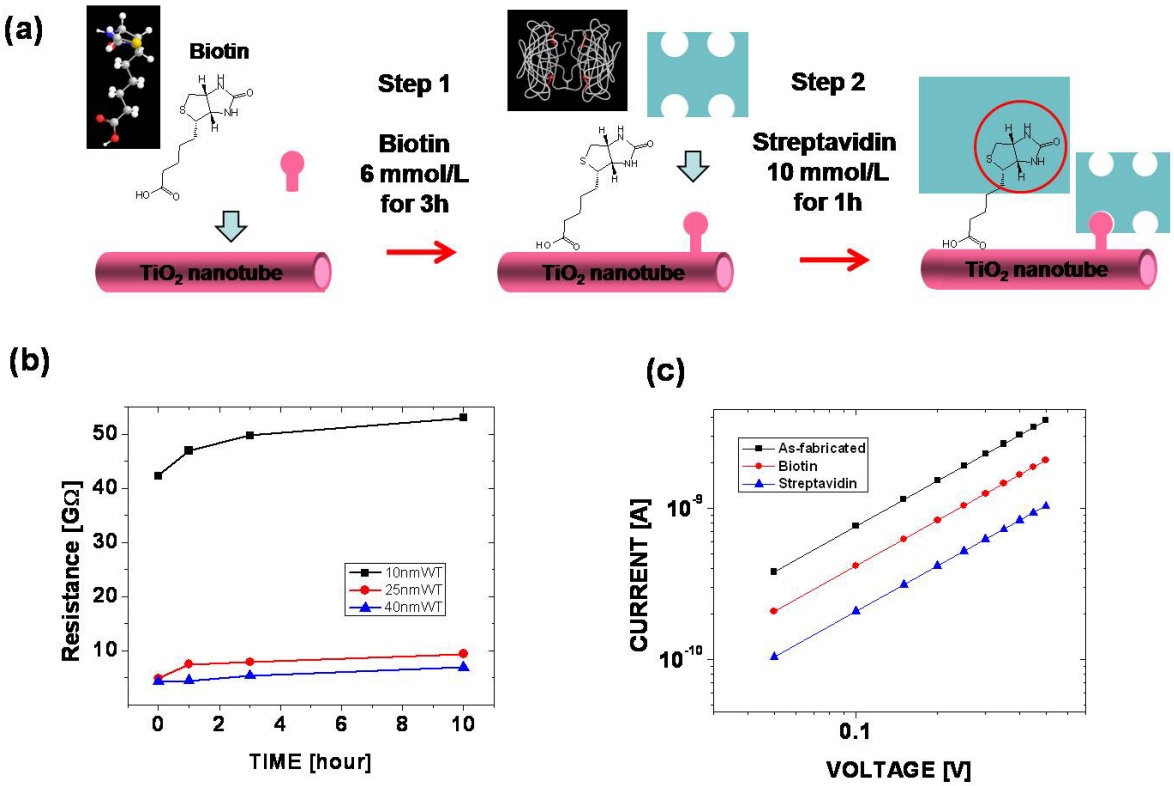

Figure 2. (a) Schematic diagram of the functionalization procedure. The surface of the TiO_2 nanotube is modified with biotin. Afterwards the functionalized surface detects streptavidin due to the strong non-covalent bond. (b) Resistance versus time curve shows that coverage of biotin is saturated after 3 hours. (c) I-V curve shows the conductance change due to depletion which is caused by biotin and streptavidin detection.

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