Sensors and Actuators B 158 (2011) 286–291

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

Low cost chemical sensor device for supersensitive pentaerythritol tetranitrate (PETN) explosives detection based on titanium dioxide nanotubes

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ARTICLE INFO

Article history:
Received 27 January 2011
Received in revised form 29 May 2011
Accepted 6 June 2011
Available online 13 June 2011

Keywords:
Explosives
Explosive detection
Nanostructures
Sensor
Sensing device

ABSTRACT

Within the last decade there has been a great increase in the need of trace and ultra-trace explosive detection. In this report, we demonstrate a new and versatile type of chemical explosive sensors based on metal oxide nanotubes easily made, even with the need of a low budget. We describe the step-by-step procedure to fabricate a sensing chip device, beginning with the synthesis of the starting materials to the point of supersensitive measurements of PETN explosive. As a result, the whole process actually is one of the most cost-effective methods to produce explosive sensing devices reported until now. The achieved chemical sensor device will be able to detect PETN explosive down to ~112 ppt.

1. Introduction

During the past years explosive-based terrorism has grown enormously, driven by the fact that explosive-based weapons have an immense damage potential and are simple and easy to deploy [1,2]. Chemical sensors designed to detect explosive vapors are awkwardly shaped, expensive and regarding their limit of detection they are in need of scientific improvement. Actually, dogs are still the most effective commercially available explosive detectors [3,4] in the fight against suicide bombers, mobile subjects and further, the removal of land mines [5,6]. Different kind of sensors used for explosive detection have been designed and engineered within the past couple of years [7–9]. Part of the major classes of energetic materials, which are used for military applications are nitroaromatics and nitramines, e.g., 2,4,6-trinitrotoluene (TNT), hexahydro-1,3,5-triazine (RDX) and pentaerythritol tetranitrate (PETN).

Due to the very low vapor pressure of TNT and PETN and hence their low concentration in air, the development of efficient and sensitive detector systems seems to be complex and expensive. However, the deployment of those systems is highly desirable, as there are considerable security needs, especially with an increased use of explosives in terrorist attacks and the present surge of international terrorism. In between, there have been miscellaneous systems and methods designed to improve the detection of explosives.

Trisha et al. developed a fluorescence turn-on mechanism to detect high explosives RDX and PETN [10]. Anderson and colleagues demonstrated that PETN could be detected using bead-based fluid arrays [11]. Mikhaltsevitch et al. explored the detection of PETN and other explosives based on polarization enhancement of NQR signals [12].

Further on, biomolecules have been employed to detect PETN. Using biomolecules, an antibody-based fluorometric assay is one of many methods that are based on resonance angle changes by biomolecular interactions that occur between immobilized antigen and antibody [13,14]. In addition, several physical detection techniques to detect explosives have been developed and used. Among other things, the most prominent methods are Raman spectroscopy, gas chromatography, cyclic voltammetry or high performance liquid chromatography [15]. While these systems are highly selective, some are not easily transportable or either portable; and most of them are very expensive. In addition, most of all systems currently used require an expert operator. Regarding production costs, high sensitivity and fast response, chemical sensing devices based on 1D nanostructures have reached strong attention in science and engineering [16–22]. Moreover, metal oxide structures seem to be promising materials for building electronic sensing devices. Nanostructures offer an extremely sensitive platform to detect molecular adsorption on their surfaces [23–26]. Inorganic nanowires and nanotubes exhibit unique electrical

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doi:10.1016/j.snb.2011.06.020

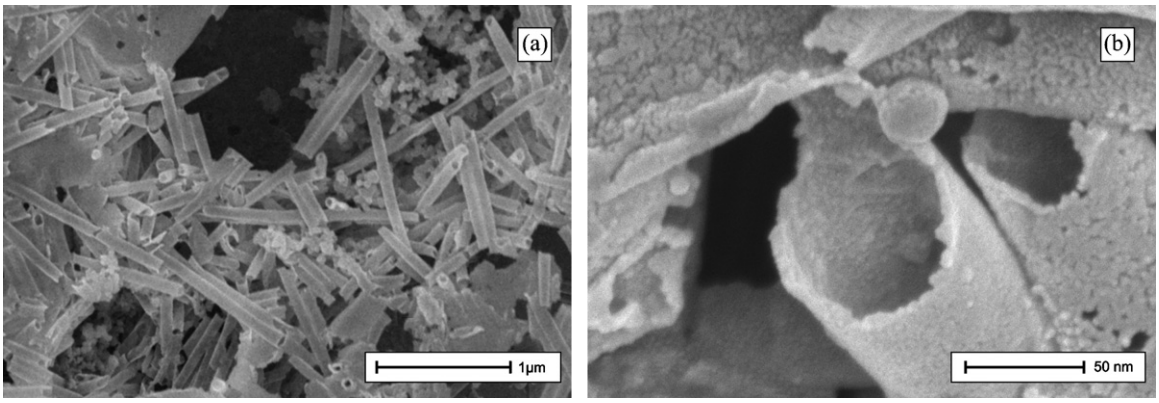

Fig. 1. (a) Ensemble of TiO_2 nanotubes dissolved out of the polycarbonate template; (b) closer image of one. TiO_2 nanotube.

properties that can be exploited for high sensitive detection devices based on molecular adsorption.

The vapor pressures of most common explosives at room temperature are extremely low and increase rapidly with ascending temperature [27]. Explosive vapors can easily be created by heating a sample. However, a very low vapor pressure alludes that these molecules are enormous adhesive and attempt to adsorb on surfaces very easily, especially on cooler surfaces. The adsorption will be higher on metals or metal oxides, due to their high surface energy. Therefore, metal oxide nanostructures yield to high sensitive explosive devices in the future.

2. Materials and methods

In this paper, we present the preparation of high sensitive PETN sensing devices, based on TiO_2 nanotubes. The reported approach offers a novel procedure to fabricate small, lightweight and one of the most cost effective sensing devices to detect PETN, which has not been reported before. The fabrication of the TiO_2 nanotube explosive sensor began with the synthesis of the TiO_2 nanotubes using a template based chemical bath deposition, according to the process which has been reported by us previously for cerium oxide and samarium oxide nanotubes [28,29]. Due to its surface limitation, chemical bath deposition is a convenient and power saving manner to engender hollow nanostructures.

To get an information about the structural properties of the synthesized nanotubes, they were examined using XRD and XPS.

The XRD measurements were performed in the reflection mode using Mo-Kα radiation (0.7107 nm). The resulting XRD pattern, shown in Fig. 1, exhibits strong diffraction peaks at 11.5° and 21.5° indicating the anatase phase of TiO_2. Further on, the peaks are in good accordance to literature data [30] describing anatase nanocrystallites.

The resulting indicated full range XPS survey spectrum is shown in Fig. 2. The spectrum exhibits all necessary Ti and O binding energies as reported previously by literature [31]. A C (1s) peak of low intensity could be observed at 285 eV that may be founded in the use of an organic template or organic solvents, used during the last steps of preparation. Beside carbon and anatase related binding energies, the spectrum do not show any further appreciable peaks of foreign elements.

The geometrical structure of the grown titanium dioxide tubes was visualized by high resolution SEM prior their deposition on a circuit as sensing material. The synthesis of the desired TiO_2 nanotubes is subdivided into three main steps, which are described as follows.

2.1. Template preparation

The template consists of polycarbonate foils with a thickness of 6–30 µm. Herein, we used off-the-shelf polycarbonate membrane filters, exposed in a very controlled way to charged particles in a nuclear reactor, sold by Whatman/GE™ and comparable companies. Due to a surface treatment with polyvinylpyrrolidone (PVP) for the commercial membrane filters, we used an additional etching process to remove the treatment.

Therefore, the off-the-shelf polycarbonate foils were chemically etched at 50 °C using a 6 N NaOH solution containing 1% sodium dodecyl sulfate [32]. The resulting pore diameter is increasing linearly with etching time; the pores are of cylindrical shape. In this report, we create templates with a pore diameter of approx. 80 nm.

2.2. Sensitization and activation

Prior to the electro-less deposition process, the surface of the polycarbonate template was treated with sensitization and activation solutions. In this way, the template surface becomes catalytically activated and deposition on the surface is possible. Best results are obtained using the following procedure. The sensitization was performed by an aqueous $SnCl_2$ solution containing 0.25 mol/L $SnCl_2$ and 0.3 mol/L hydrochloric acid for approx. 30 min at 45 °C. After rinsing the sensitized template with deionized water for 1 min, it was placed in the aqueous activation solution containing 0.15 mol/L $AgNO_3$ and 0.01 mol/L $Co(NO_3)_2$ for a minimum of 10 min, followed by rinsing in deionized water for 1 min. To

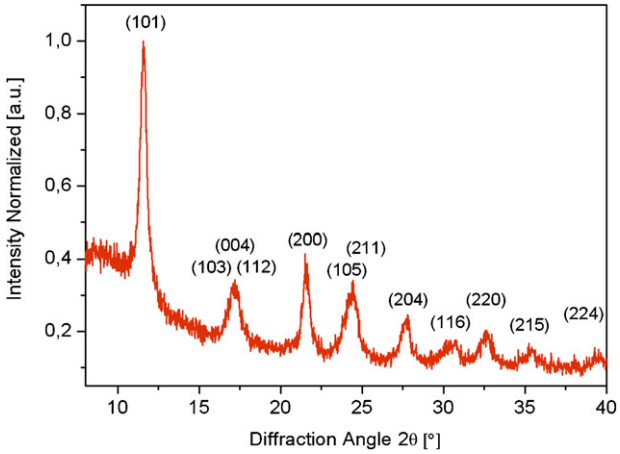

Fig. 2. Diffraction pattern of the synthesized TiO_2-nanotubes used for the PETN-sensing device.