

# Platinum functionalized Titania Nanotube Array Sensor for Detection of Trichloroethylene in Water

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**Abstract**—A sensor using platinum functionalized titania nanotubes for the detection of Trichloroethylene (TCE) in water samples has been developed. The titania nanotubes were synthesized using an electrochemical anodization technique and platinum was photocatalytically deposited on the nanotubes. The sensor exhibits a good response to TCE concentrations in the range of 10 to 1000 ppm.

## I. INTRODUCTION

Chlorinated solvents are a type of chemical that is used in industrial processes (i.e. Aerospace and Electronics Industry, Dry Cleaning) and common household consumer products. They are found in products such as shoe polish, degreasers, waxes, pesticides, drain cleaners and oven cleaners. Unfortunately these chemicals have found their way into groundwater contaminating water sources around the United States and around the world [1]. This is a problem due to the associated toxic and carcinogenic effects these compounds have on the general population [2]. The Environmental Protection Agency (EPA) has estimated that volatile organic compounds (VOCs) are found in an estimated one-fifth of United States water supplies [3]. According to the US Geological Survey estimates, VOC levels were found to be in excess of federal drinking water criteria in about 6 percent of urban wells and 1.5 percent of rural wells. Among VOCs, Trichloroethylene (TCE) is a major ground-water pollutant and found to be present in about 1400 military properties around the US [4]. The actual amount of human exposure to the VOCs like TCE remains uncertain, pointing to a need for point-of-use TCE sensor [5].

The detection of TCE-gas (air, nitrogen, oxygen, argon) mixtures has been widely reported with detection limits in range of pph (parts-per-hundred) [5], down to 1 ppm (parts-per-million) [6]. However, the operating temperatures of these sensors are in the range of 100-400 °C [7], making it power intensive and less amenable for field-based sensing. None of the above sensors have been used to detect TCE levels in water based samples.

Conventional methods for detection of VOCs from water are traditionally performed in central laboratories using sophisticated lab equipment such as gas chromatography (GC) and mass spectroscopy (MS). While these methods are highly sensitive and quantitative, they are not appropriate for field use due to the complexity of the instrument and cost. It is

not possible to detect TCE in water using electrochemical methods with a conventional precious metal working electrode, since the reduction potential of TCE is much higher than water. TCE sensors using immobilized microbial membrane have been widely reported and have excellent sensitivity [8], [9]. But these sensors suffer from issues such as complicated preparation process, a long response time and a short shelf-life time [10]. Chen et al. reported a lead modified Platinum-Titanium thin film with detection limit of 100 ppm for TCE in water [11].

Oxide semiconductor nanomaterials have been shown to be effective in detecting VOCs due to their high specific surface area and good selectivity [12]. Titania nanotube array (TNA) have received significant interest due to ease of synthesis and tunable size (nanotube diameter and length) over other methods [13]. Sensors based on TNA have been demonstrated in the detection of gases such as hydrogen, oxygen and organic vapors like toluene, ethanol and formaldehyde [14]–[17]. In this work, detection of TCE in water using Platinum (Pt) functionalized TNA (Pt/TNA) (Figure 2) has been discussed. The TCE is purged from the water using a carrier gas (air) and carried over to the Pt/TNA sensor. When the TCE in carrier air reacts with the Pt functionalized nanotubes, an order of magnitude change in current is measured using a simple potentiostat. This change in current is correlated to the level of TCE present in solution. The sensitivity ( $S$ ) of the Pt/TNA sensor is calculated as the ratio of change in current ( $I_{TCE\ in\ water}$ ) when the TCE-water vapor mix is introduced to the baseline current in air ( $I_{Air}$ ):

$$S = \frac{I_{TCE\ in\ water}}{I_{Air}} \quad (1)$$

## II. MATERIALS AND METHODS

### A. Fabrication of TNA

TNA were synthesized by electrochemical anodization similar to previously reported protocols [18]. In summary, Ti foils (0.1 mm thick) were anodized under magnetic stirring in an electrolytic solution consisting of ethylene glycol (Fisher Scientific, Waltham, MA), deionized (DI) water (3 wt. %) and ammonium fluoride (0.5 wt.%, Fischer Scientific). A two-electrode configuration with platinum (Pt) foil as the cathode

was used for anodization. The anodization was carried out at an applied potential of 45 V(D.C.) (Agilent, E3647A) for 60 minutes and subsequently annealed in oxygen ( $O_2$ ) at  $500^\circ C$  (ramp up at a rate of 1.6 C/min from  $25^\circ C$ ) for 2 hours.

### B. Pt functionalization of TNA

The annealed TNA were functionalized with metallic Pt nanoparticles via photocatalytic reduction of chloroplatinic acid [19]. Annealed TNA were immersed in a 2mM solution of chloroplatinic acid ( $H_2PtCl_6 \cdot 6H_2O$ ) (Aldrich), in a 50/50 mixture of methanol and water, then subject to UV irradiation (365 nm, 100-W UV lamp) for one hour [20]. The Pt ions in solution are reduced at the TNA surface to form metallic platinum deposits (5-10 nm) as seen in Figure 2. The methanol in solution serves as a scavenger of photo-induced holes. Functionalization of the sensor using nanosized Pt catalyst has shown to improve the response of semiconductor sensors during detection of VOCs [6]. Subsequent to the deposition, one side of the Pt/TNA strip was polished manually with sandpaper and washed in DI water to remove the Pt-Nanotubes and to expose the underlying bare Titanium (Ti) metal (in effect forming a Pt on nanotubes on Ti structure). The morphology of TNAs after functionalization with Pt was analyzed using a field emission scanning electron microscope (FESEM) (Hitachi, S-4800). Energy dispersive x-ray spectroscopy (EDX) analysis of a 25 by 20  $\mu m$  area of the sample was obtained using an Oxford detector. X-ray diffraction (Rigaku MiniFlex 600) was used to confirm the crystalline phases of the annealed Pt/TNA.

### C. Amperometric detection of TCE

The experimental setup for detection of TCE in water is shown in Figure 1. It comprised of an inlet air, a mass flow controller (MFC), potentiostat and detection chamber. The sensor, a 50  $mm^2$  Pt/TNA strip connected via alligator clips to the external potentiostat (Gamry Reference 600) is placed inside the detection chamber. A low bias voltage of -1 V (two electrode system) is applied using the potentiostat and the current response is measured. Different concentrations of TCE in DI water were prepared in a Büchner flask (250 ml). Air (at 120 Standard Cubic Centimeters per Minute/SCCM controlled using MFC) was bubbled through the respective TCE-DI water solution for 15 seconds and delivered to the sensor through a brass nozzle. This is similar to the protocol used for purging VOCs from water based samples for detection in a Purge and Trap GC/MS system. The TCE-DI water solution was heated to  $50^\circ C$  to enhance TCE transport from the solution to air. After the 15 second detection interval, TCE-DI water vapor flow is cut and air is introduced over the sensor. Experiments were also run with air bubbled through DI water as a negative control (0 ppm TCE). All experiments were conducted at room temperature.

## III. RESULTS

The FESEM images of TNA functionalized with Pt and annealed in  $O_2$  are shown in Figure 2. The nanotubes are approximately 1-1.4  $\mu m$  in length, with a pore diameter of

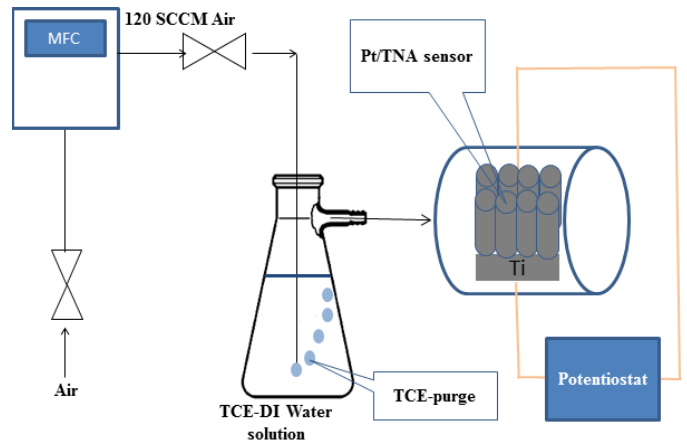


Fig. 1. Experimental set-up for TCE detection. TCE-DI water mixture is placed in a Büchner flask. Air at 120 SCCM is bubbled through the solution and delivered to the Pt/TNA sensor

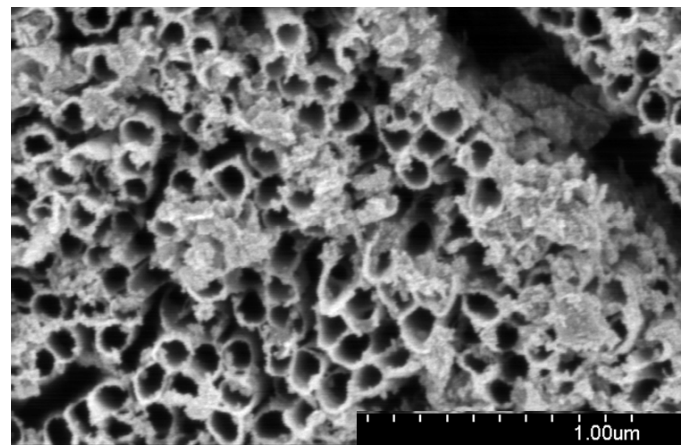


Fig. 2. TNA functionalized with Pt. The deposited Pt particles as well as agglomerates are seen on the walls of TNA

90-100 nm and tube wall thickness of 10-20 nm. From the images, the photocatalytically deposited Pt particles as well as agglomerates can be seen on the walls of TNA. EDX analysis (Figure 3) shows the percentage of Pt to be about 0.3 % wt. in addition to presence of titanium, oxygen and carbon. The presence of carbon is due to anodization in ethylene glycol solution [18].

X-ray diffraction patterns of  $O_2$  annealed TNA samples (not shown) confirmed the predominantly anatase phase  $TiO_2$ . TNA samples annealed at  $400-500^\circ C$  in ( $O_2$ ) have shown to exhibit higher sensitivity of gases like formaldehyde compared to as-prepared (amorphous) TNA samples [17].

Figure 4 shows the current response of the Pt/TNA sensor, when air is bubbled through 10 ppm TCE solution to the sensor. During the Stage I, air (120 SCCM) is introduced over the sensor and the current response represents the baseline ( $I_{Air}$ ). During the Stage II, air bubbled (at 120 SCCM) through 10 ppm TCE-DI water solution is introduced over the sensor for 15 seconds. An instantaneous (<10 seconds) increase in current response is seen and reaches a maximum value

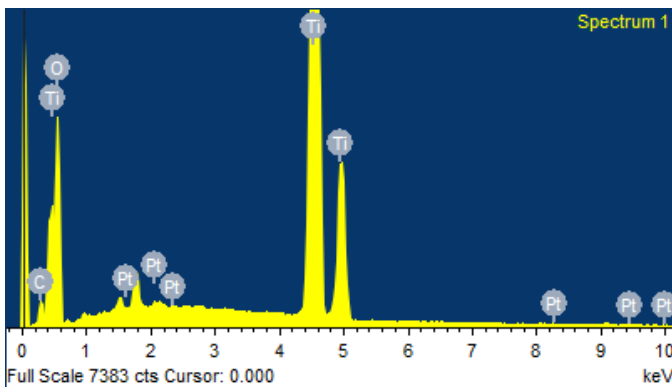


Fig. 3. EDX analysis of the sample showing presence of Pt

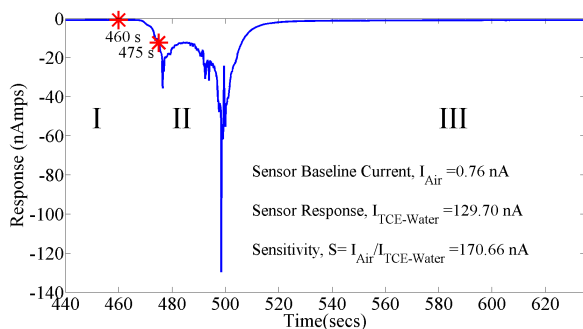


Fig. 4. Potentiostatic ( $I$  vs.  $t$ ) response of Pt/TNA sensor to 10 ppm TCE in water. A representative cycle of 120 s is shown in the figure. The cycle is divided into three stages. Stage I shows the baseline current when air is introduced over the sensor. The current increases (Stage II) when TCE-water vapor is introduced over the sensor for 15 seconds ( $t=460$  to 475 seconds). An instantaneous increase in current response is noticed. The current starts to drop after 40 seconds ( $t=500$  seconds) and drops to 10% of original value after 170 seconds ( $t=633$  seconds) (Stage III)

( $I_{TCE\ in\ water}$ ). Subsequently, the current starts to decrease and goes back to the baseline current after 170 seconds. Figure 5 shows the sensitivity (equation (1)) of the Pt/TNA sensor to different concentrations of TCE in water, ranging from 0 ppm to 1000 ppm. The response time (time taken for the sensor to reach maximum current from the time of injection of air through solution) is around 38 seconds. The non-zero value of response at 0 ppm TCE is likely due to the presence of dissolved gases in adsorbed water molecules on the sensor surface, which are known to change the conductivity of metal oxide sensors [17].

The sensing mechanism of Pt/TNA is based on the reaction of TCE with the chemisorbed reactive oxygen species (primarily  $O^-$ ) on the surface of the sensor [7], [21]. This reaction leads to a pooling of electrons and causes a change in conductance through the sensor which leads to a change in current. The reaction of TCE with adsorbed  $O^-$ , for example, is expressed as:



The higher specific surface area of TNA helps increase the

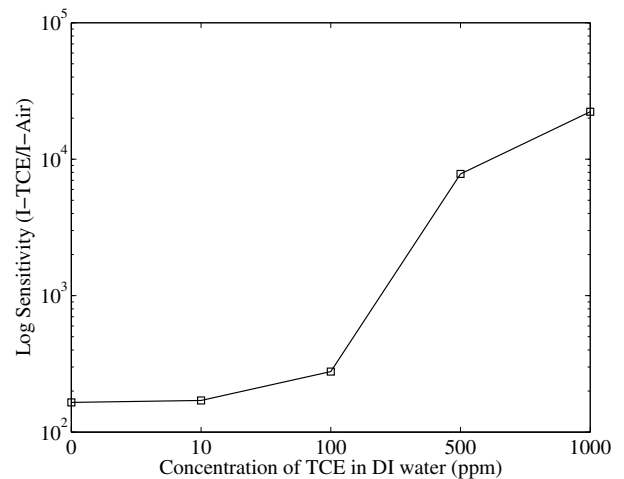


Fig. 5. Log plot of Pt/TNA sensor sensitivity to TCE concentrations (0-1000 ppm in water)

sensitivity to TCE due to increased amount of chemisorbed  $O_2$  via enhanced diffusion.

The Pt deposited on TNA (semiconductor oxide) forms a Schottky contact [22], [23]. This results in an alignment of the Fermi-surface of  $TiO_2$  and Pt, inducing band-bending, leading to a reduction of Schottky-barrier height [22]. This decrease in barrier height could be the reason for good response of the Pt/TNT sensor to TCE at room temperature operation.

#### IV. CONCLUSION

In summary, a Pt functionalized TNA sensor for detection of TCE in water sample is reported. The sensor operating at room temperature shows response to TCE in water at concentrations ranging from 10 ppm to 1000 ppm. This is in the concentration range of TCE contamination in sites around the United States [24], [25] and hence can be easily incorporated into a field-based sensor.

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