

SELF-REGENERATING PHOTOCATALYTIC SENSOR BASED ON DIELECTROPHORETICALLY ASSEMBLED TiO₂ NANOWIRES FOR POLLUTANT VAPOR SENSING

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ABSTRACT

This paper reports an improved TiO₂ based vapor sensor fabricated by dielectrophoretically assembling TiO₂ nanowires. With incorporating a parallel laminar flow field with AC electric fields, the dielectrophoresis of TiO₂ nanowires in ethanol was systematically studied at varied AC frequencies and flow rates. With the aid of UV light, the developed vapor nanosensors can detect vapor pollutants including NH₃, acetone and ethanol at room temperature. The detection limit, the response time, and the recovery time of the developed vapor nanosensors are 10 ppm, 120 seconds, and 60 seconds, respectively.

KEYWORDS

TiO₂ nanowires, dielectrophoretical assembly, vapor sensing, nanosensor.

INTRODUCTION

TiO₂ based vapor sensor has been attracted increasing attention throughout the past years due to its advantages including high sensitivity, low cost, rapid response, and recovery. However, conventional TiO₂ based vapor sensor was usually operative at higher temperature (>300°C) thereby limits its practical application [1]. Therefore, new approaches are highly demanded to make the vapor sensor operated at low or room temperature [2]. Furthermore, developing a method with well controllability of the assembling of TiO₂ nanostructures is of great importance, because the morphology of the assembled TiO₂ nanostructures (nanowires, nanotubes, nanorods or nanobelts) used for vapor sensing is a key to its performance. In the current paper, we fabricated vapor sensors by dielectrophoretically assembling TiO₂ nanowires and applied UV light to make the sensor operated at room temperature. The sensing mechanism used in our system is schematically illustrated in Fig. 1. Under UV light, the semiconducting TiO₂ nanowires could generate electrons and electron holes which can catalyze the oxidation of molecules such as NH₃ and acetone exemplified in Fig. 1. The diffuse of oxygen outwards towards TiO₂ nanowires will result in a decrease of vacancies and an increase in resistance that is correlated to organic vapor concentration.

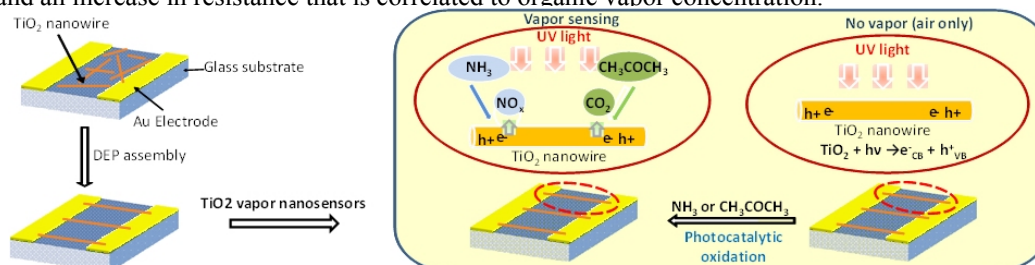


Figure 1. Schematic drawing of the developed self-regenerating photocatalytic sensor based on dielectrophoretically assembled TiO₂ nanowires for pollutant vapor sensing.

DESIGN AND FABRICATION

The diagram of microelectrodes with the coplanar structure fabricated by photolithography technique is shown in Fig. 2. Two electrode designs with gap distances of 10 and 20 μm were used in the current study. TiO₂ nanowires were synthesized by the ethylene glycol (EG)-mediated method [3]. Specifically, 0.050 mL titanium (IV) butoxide was added to a 50 mL flask that contained 10 mL EG and the solution was heated to 170 °C under stirring for 2 h. The white flocculate was harvested using centrifugation, followed by washing with deionized water and ethanol several times to remove excess EG from the sample. Once collected, the glycolate nanowires were calcined into anatase TiO₂ nanowires at 500°C for 3 h. The morphology of synthesized TiO₂ nanowires observed by SEM was shown in Fig. 3, indicating 550 nm in mean diameter and 26 μm in mean length.

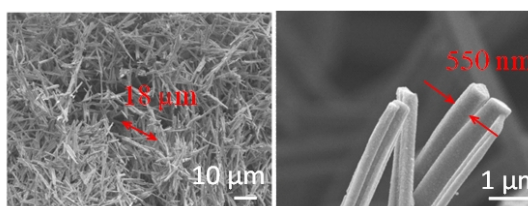
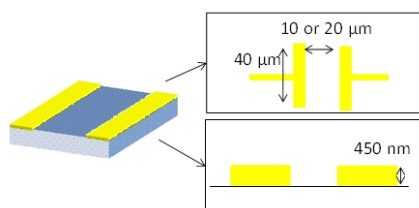


Figure 2. Diagram of the fabricated microelectrodes used for DEP assembly.

Figure 3. Scanning electron microscopy (SEM) images of synthesized TiO₂ nanowires.

EXPERIMENTAL RESULTS

The experimental setup for dielectrophoretically (DEP) assembling TiO₂ nanowires was schematically illustrated in Fig. 4. To gain the controllability of the assembling and prevent the precipitation of TiO₂ on the electrode surface, a laminar flow parallel to the direction of the electric field was applied using a syringe pump. The synthesized TiO₂ nanowires were dispersed in ethanol with a concentration of 0.1% (wt%) for DEP assembling. In the current study the applied AC electric field intensity was kept constant at 500 V/mm while the AC frequency and flow rate were varied. The assembling process was in-situ monitored by optical microscope and the morphology and number of assembled TiO₂ nanowires were characterized by OM and SEM.

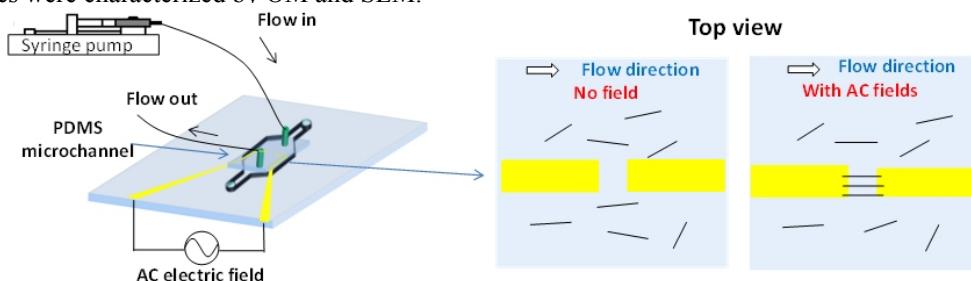


Figure 4. Schematic of DEP assembly of TiO₂ nanowires under laminar flow. The flow field was applied to control the DEP assembling process.

At constant electric field intensity of 500 V/mm and AC frequency of 10 kHz, the morphologies of dielectrophoretically assembled TiO₂ nanowires at varied flow rates were exhibited in Fig. 5. It is clearly observed at high flow rate less TiO₂ nanowires were assembled across the electrodes. The strong dependence of DEP assembly on flow rate is clearly exhibited in Fig. 6(a). At the flow rate of 10 $\mu\text{L}/\text{min}$ no nanowire was assembled because the strong hydrodynamic force exerted on the nanowires at high flow rate overwhelmed the DEP force. The DEP assembling was also dependent on the AC frequency of applied field, as Fig. 6(b) indicates that the assembling is effective only when the frequency is below 100 kHz. At low frequencies, the DEP force is dominated by the surface conductance of the TiO₂ nanowires that is higher than the water medium thus is positive, i.e., inducing the TiO₂ nanowires to the high field regions. In contrast, at high frequencies, the DEP force is dominated by the permittivity of TiO₂. The resulted negative DEP leads TiO₂ nanowires depleted from the electrodes which are high electric field regions. A key advance of the current paper over the previous studies lies in the incorporation of the laminar flow with the DEP assembly. Without flow the nanowires precipitated rapidly and accumulated between electrodes by DEP force in an uncontrolled manner. It is clearly indicated in Fig. 6 that controllability over the number of assembled TiO₂ nanowires was successfully achieved.

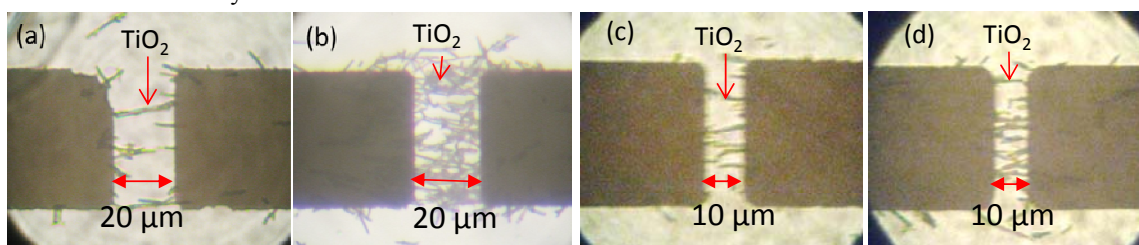


Figure 5. Optical images for typical DEP-flow assembly of TiO₂ nanowires in ethanol for 5 min under constant voltage of 10 V and AC frequency of 10 kHz with varying flow rate: (a) 10 $\mu\text{L min}^{-1}$ and (b) 1 $\mu\text{L min}^{-1}$ with gap distance between electrodes of 20 μm ; (c) 10 $\mu\text{L min}^{-1}$ and (d) 1 $\mu\text{L min}^{-1}$ with electrode gap distance of 10 μm .

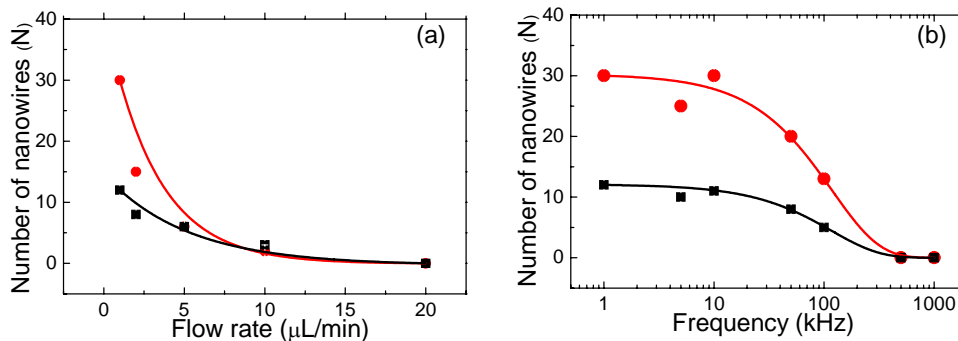


Figure 6. (a) Effect of flow rate on the number of DEP-flow assembled TiO₂ nanowires for 5 min under constant voltage of 10 V and AC frequency of 10 kHz across electrodes with gap distance of 10 (●) and 20 μm (■). (b) Effect of AC frequency on the number of DEP-flow assembled TiO₂ nanowires for 5 min under constant voltage of 10 V and flow rate of 1 $\mu\text{L min}^{-1}$ across electrodes with gap distance of 10 (●) and 20 μm (■).

Fig. 7(a) shows the electrical impedances of assembled nanowire arrays with varied number of TiO₂ nanowires measured by impedance analyzer. The sensing experiments of the assembled TiO₂ nanowires were conducted at the

constant AC frequency of 10 kHz with measuring the impedance change. The sensing results of the fabricated sensor made of two assembled TiO₂ nanowires across 20 μm to varied vapors were shown in Fig. 7(b). When UV light was absent, the impedance of the sensor didn't exhibit any detectable change upon purging varied organic vapors including NH₃, acetone, and ethanol vapors. The insensitivity of the sensor without UV light is due to the low electron and vacancy densities of TiO₂ nanowires at room temperature. When UV light with wavelength of 365 nm and intensity of 6 mW/cm² was applied, the measured impedance shows a significant increase as NH₃, acetone and ethanol vapors with 100 ppm concentration were purged into the device. The sensitivity of the sensor towards varied vapors appears to follow the order that ethanol > acetone ≈ NH₃. When the air was purged into the sensor, within 60 seconds the measured impedance returned to its initial value, indicating an excellent self-regenerating ability of the developed vapor sensors.

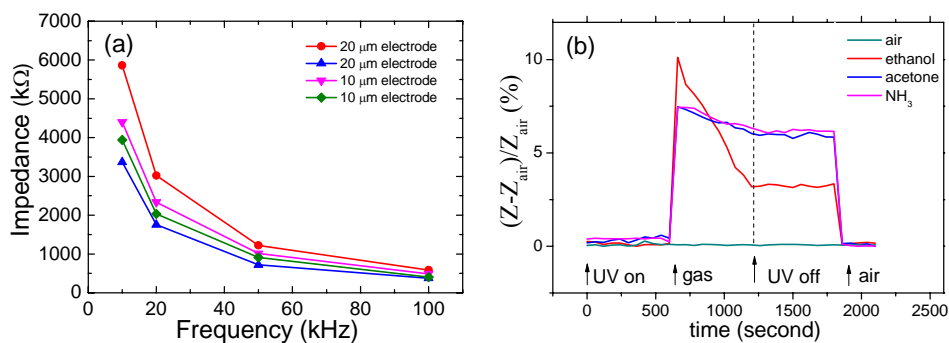


Figure 7. (a) Impedances of assembled TiO₂ nanowires. (b) Response and recovery of the fabricated sensor made of two TiO₂ nanowires across 20 μm gaped electrodes to varied vapors with concentration of 100 ppm.

The limit of detection (LOD) of the fabricated sensor to NH₃ was measured. Fig. 8 (a) and (b) shows the decreases in impedance of two sensors to NH₃ at concentrations ranging from 10 to 100 ppm. The sensitivity of the sensor of TiO₂ nanowires on 10 μm gaped electrodes was higher than that of the nanowires on 20 μm gaped electrodes, which is reasonable considering the number of TiO₂ nanowires was higher on 10 μm gaped electrodes. Fig. 8 (c) shows that the LOD of the sensor on 10 μm gaped electrodes was measured to be as low as 10 ppm at room temperature.

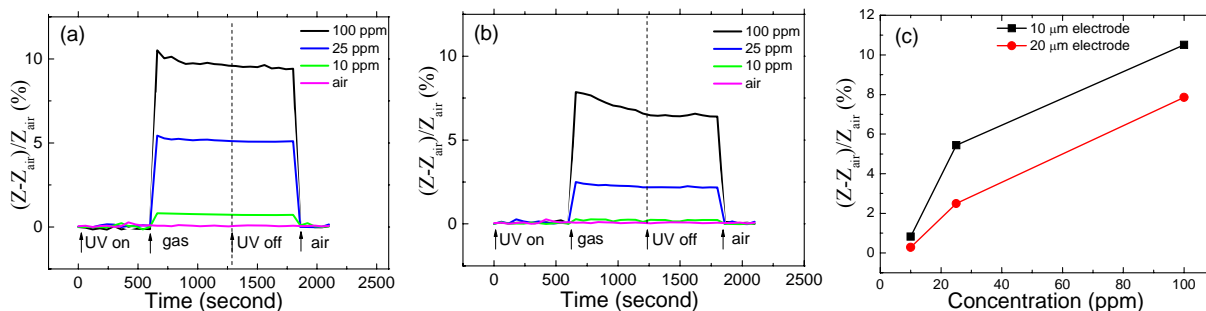


Figure 8. (a) Response of the fabricated sensor made of 10 TiO₂ nanowires across 10 μm gaped electrodes at room temperature to NH₃ with varied concentration. (b) Response of sensor made of 2 TiO₂ nanowires across 20 μm gaped electrodes to NH₃. (c) Response of the two fabricated sensors and limit of detections to NH₃ at room temperature.

CONCLUSIONS

Vapor sensors were fabricated by dielectrophoretically assembling TiO₂ nanowires with the help of fluid flow. Under UV light, the sensors showed high sensitivity (LOD of 10 ppm to NH₃), fast response (120 sec) and fast recovery (60 sec) to vapor pollutants including NH₃, acetone and ethanol at room temperature.

ACKNOWLEDGEMENT

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