

Article

Preparation, Characterization and Sensitive Gas Sensing of Conductive Core-sheath TiO₂-PEDOT Nanocables

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Abstract: Conductive core-sheath TiO₂-PEDOT nanocables were prepared using electrospun TiO₂ nanofibers as template, followed by vapor phase polymerization of EDOT. Various techniques were employed to characterize the sample. The results reveal that the TiO₂ core has an average diameter of ~78 nm while the PEDOT sheath has a uniform thickness of ~6 nm. The as-prepared TiO₂-PEDOT nanocables display a fast and reversible response to gaseous NO₂ and NH₃ with a limit of detection as low as 7 ppb and 675 ppb (S/N=3), respectively. This study provides a route for the synthesis of conductive nanostructures which show excellent performance for sensing applications.

Keywords: poly(3,4-ethylenedioxythiophene); nanocables; gas sensor; vapor phase polymerization; electrospinning

1. Introduction

Controllable synthesis of conducting polymer nanostructures has been intensively investigated in the past decades due to their unique optical and electronic properties. Among various methods in the synthesis of conducting polymer nanostructures, the template method is the most efficient and controllable one [1,2]. Various templates such as carbon nanotubes and anodic alumina oxides have

been used to provide scaffold/support or spatial confinement for the growth of desired conducting polymers [3-5]. Recently, electrospun nanofibers have emerged as ideal supporting templates in the fabrication of core-sheath nanostructures with a narrow diameter distribution because the deposition of conducting polymers on electrospun nanofibrous template could potentially yield a class of nanomaterials with a large surface to volume ratio, highly porous structure, and an ultrathin conducting layer, which favor the gas adsorption/desorption process and thus make such materials attractive as potential sensing elements [6,7].

It has been well documented that conducting polymers are sensitive to environmental compositions [8]. Among the commonly used conducting polymers, poly(3,4-ethylenedioxythiophene) (PEDOT) has attracted a lot of attention in recent years due to its excellent properties such as long-term stability, high conductivity, optical transparency in its doped state, low band gap, and moderate redox potential [9-12]. PEDOT is commonly accepted to be more environmentally stable than other conducting polymers such as polypyrrole and polyaniline [13,14]. These features make PEDOT and its derivatives appealing in gas sensing. To date, numerous PEDOT based gas sensors have been proposed to detect gaseous analytes such as NH_3 [15-19], HCl [15,16], alcohol [20,21], and NO [22]. To synthesize PEDOT for such applications, electrochemical polymerization and chemical polymerization are widely used. Compared with electrochemical polymerization, chemical polymerization of EDOT can provide uniform coating on both conducting and non-conducting surface, requires relatively simple equipment, and adapts a flexible procedure; therefore, it has been widely employed to deposit PEDOT on different substrate [1,23].

Recently, a conducting polymer such as polypyrrole has been successfully coated on nanofibers and its application for ultrasensitive NH_3 detection has also been demonstrated [6,24]. Herein, we report a facile method to fabricate conductive core-sheath TiO_2 -PEDOT nanocables by vapor phase polymerization of EDOT. Electrospun TiO_2 nanofibers were used as the template. Various characterization techniques were applied to characterize the as-prepared samples and the results reveal that the TiO_2 core has an average diameter of ~ 78 nm, while the PEDOT sheath has a uniform thickness of ~ 6 nm. We further demonstrated the application of the TiO_2 -PEDOT nanocables for NO_2 and NH_3 detection. The as-fabricated sensor exhibits fast response and good recovery upon exposure of gaseous analytes and also shows excellent limit of detection. This study provides a simple strategy to fabricate conductive nanomaterial, which is promising in various sensing applications.

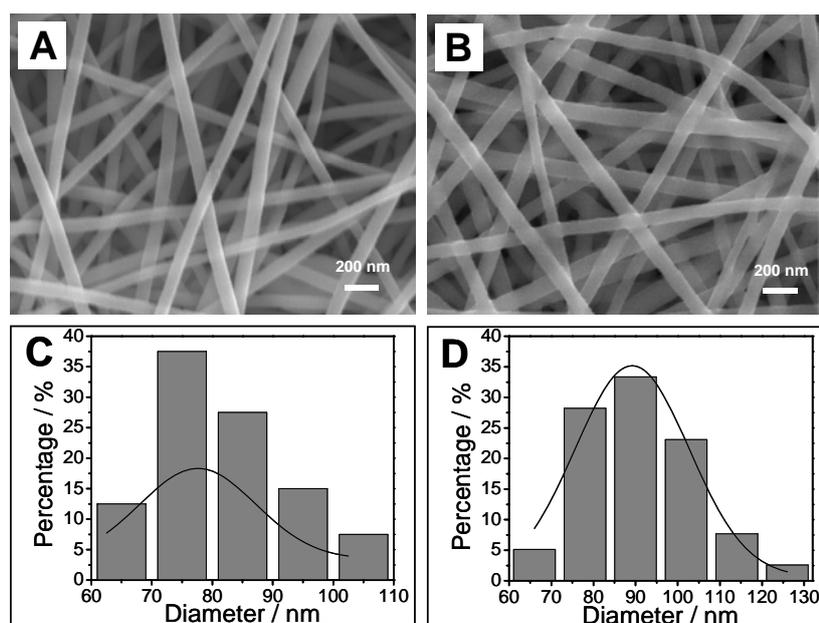
2. Results and Discussion

2.1. Characterization of Conductive Core-sheath TiO_2 -PEDOT Nanocables

Electrospinning is a straightforward and versatile technique to produce continuous fibers with nanoscale diameter and a large surface to volume ratio [25]. In this research, TiO_2 is chosen as template in the preparation of conductive TiO_2 -PEDOT nanocables due to its excellent chemical stability in oxidizing environments. Figure 1A shows the typical SEM image of the as-prepared TiO_2 nanofibers. It is clearly seen that the sample consists of numerous randomly-oriented nanofibers with relatively uniform morphology and size in the area examined. When the white TiO_2 nanofibers were dipped into FeCl_3 -ethanol solution and dried in air, their color became yellowish due to the adsorption of FeCl_3 . After the sample was exposed to EDOT vapor at 95°C [26], the adsorbed FeCl_3 triggered the

vapor phase polymerization of EDOT. One obvious phenomenon is that the sample became dark blue, indicating the formation of PEDOT on the surface of TiO₂ nanofibers. Figure 1B reveals that the morphology of the as-prepared conductive TiO₂-PEDOT nanocables is similar to that of TiO₂ nanofibers and only the diameter is slightly bigger than that of corresponding TiO₂ nanofibers. Diameter distributions for the samples before and after PEDOT coating were further obtained using 40 randomly chosen TiO₂ nanofibers and TiO₂-PEDOT nanocables in corresponding SEM images and then analyzed by Gaussian fitting. One can see from Figures 1C-D that more than 85% of the TiO₂-PEDOT nanocables have diameters ranging from 72 to 108 nm with a Gaussian mean diameter of 89.2 nm, while the diameter of TiO₂ nanofiber template has a Gaussian mean value of 77.6 nm. As the difference of the two Gaussian mean diameters is 11.6 nm, which is equal to twice of the thickness of PEDOT sheath, the thickness of the coated PEDOT layer is calculated to be ~5.8 nm.

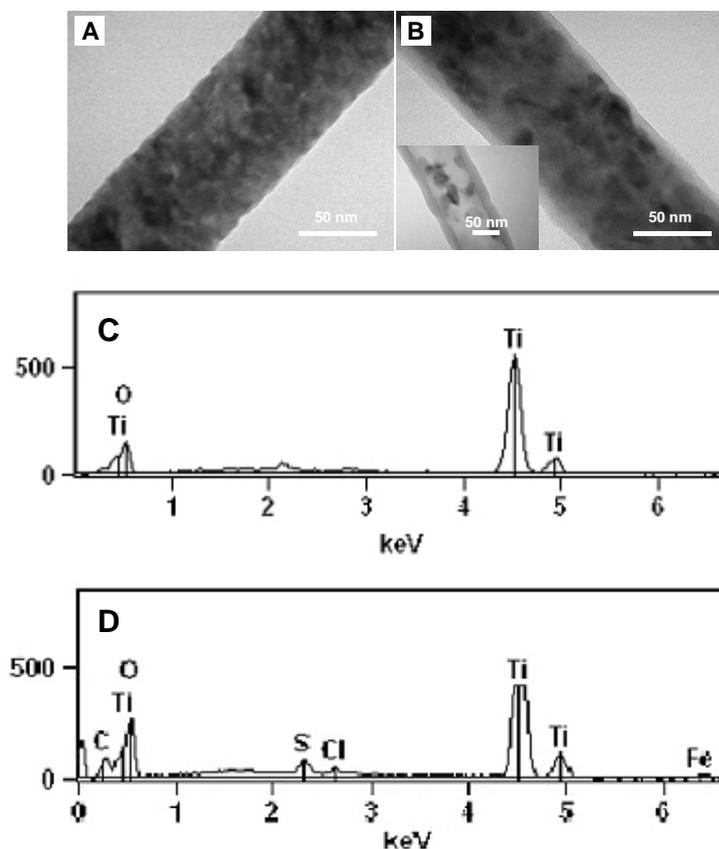
Figure 1. (A) SEM image of electrospun TiO₂ nanofibers. (B) SEM image of TiO₂-PEDOT nanocables after the vapor phase polymerization of PEDOT on TiO₂ nanofibers. (C) and (D) Histograms showing the size distribution of TiO₂ nanofibers and TiO₂-PEDOT nanocables, respectively.



The detailed morphology of the samples were further characterized and analyzed by TEM. Figure 2A and B show typical TEM images of the TiO₂ nanofiber before and after PEDOT-coating. Clearly seen from the TEM images, TiO₂ nanofiber has a rough surface and consists of many nanoparticles (Figure 2A), while TiO₂-PEDOT nanocable displays a core-sheath structure with an extremely thin (~6 nm) layer of PEDOT (Figure 2B), which is in good agreement with the analysis of Gaussian fitting previously. The TEM images also clearly indicate the uniformity of TiO₂ core as well as the uniformity and continuity of PEDOT sheath. In addition, the vapor polymerization of EDOT using FeCl₃ as an oxidant would not transform the morphology of the electrospun TiO₂ nanofibers. It has been reported that TiO₂ could be dissolved in HF solution [27]. In order to better reveal the core-sheath structure after PEDOT-coating, the as-prepared TiO₂-PEDOT nanocables were soaked into

a 5 mol/L HF solution under overnight-sonication to selectively remove TiO₂ cores. It can be seen that a tubular structure was indeed observed after the dissolution of TiO₂ cores. However, the PEDOT layer after HF treatment is thicker than that before treatment (inset of Figure 2B). A similar phenomenon has been observed by other group [28] and it may be attributed to the irreversible swelling-effect of PEDOT in solution. Compared to conventional PEDOT films prepared by chemical polymerization [29,30], the as-prepared PEDOT layer is much thinner, which may be attributed to the limited adsorption of oxidant FeCl₃ on TiO₂ surface. Such ultrathin PEDOT layer makes it promising in various sensor applications. The composition change during the PEDOT-coating process could also be revealed by EDX analysis. Figure 2C reveals that the TiO₂ nanofibers are only composed of elements of titanium and oxygen. No other peak was observed, indicating that the PVP used in the electrospinning has been completely removed by calcination. The EDX peaks were further fitted by Chi-squared filter applying the Proza (Phi-Rho-Z) correction method, and the calculated ratio of Ti to O was an approximate 1:2, in good agreement with the stoichiometric proportion of TiO₂. In contrast, peaks associated with carbon and sulfur were observed for the sample after PEDOT-coating (Figure 2D), indicating the formation of PEDOT. The iron and chlorine were also identified in the PEDOT-coated sample, which was reasonable as FeCl₃ was used as the oxidant and Fe and Cl were left in the PEDOT layer after the vapor phase polymerization.

Figure 2. (A) TEM image of an individual TiO₂ nanofiber. (B) TEM image of a core-sheath TiO₂-PEDOT nanocable. The inset shows PEDOT nanotube obtained by selectively removing TiO₂ core in 5 mol/L HF aqueous solution. (C) EDX element analysis result for TiO₂ nanofibers. (D) EDX element analysis result for TiO₂-PEDOT nanocables.



The formation of PEDOT on TiO_2 was further confirmed by the FTIR spectra (Figure 3). The TiO_2 nanofibers have the main bands between 400 and 700 cm^{-1} , which are attributed to Ti–O stretching and Ti–O–Ti bridging stretching modes [31]. In addition, no band related to CH stretching of hydrocarbon was observed, indicating that PVP has been removed by calcination at $500\text{ }^\circ\text{C}$. After PEDOT-coating, the characteristic bands corresponding to PEDOT were observed in the range of 900 – 1520 cm^{-1} . Specifically, the peaks at around $1,520$ and $1,344\text{ cm}^{-1}$ can be assigned to C=C and C–C stretching mode of thiophene ring, respectively, while the peaks centered at $1,208$, $1,145$, and $1,093\text{ cm}^{-1}$ are ascribed to C–O–C bond stretching in the ethylene dioxy group. The peaks at 985 and 834 cm^{-1} can be assigned to C–S bond in the thiophene ring. It has also been reported that C–S bond usually have another peak at $\sim 682\text{ cm}^{-1}$. However, this peak was not observed in FTIR spectrum of TiO_2 -PEDOT, and it may be concealed by the intense TiO_2 peak in the same region. The presence of water and hydroxy groups was also manifested, as the existence of a bending mode of H–O–H at $1,635\text{ cm}^{-1}$ and a strong stretching vibration of O–H at $3,440\text{ cm}^{-1}$, which can be attributed to the moisture bound to the samples and/or the possible presence of reduced oxidant salt species FeCl_2 in a hydrate form [6]. Both IR spectra of TiO_2 -PEDOT nanocables and TiO_2 nanofibers were in good agreement with the literature [26,31–33]. It is noteworthy that the strong TiO_2 peaks in the region between 400 – 700 cm^{-1} are observed for both samples and the PEDOT coating cannot conceal their presence, indicating that PEDOT sheath is ultra-thin, in good agreement with TEM results.

Figure 3. FTIR spectra of the electrospun TiO_2 nanofibers and TiO_2 -PEDOT nanocables.

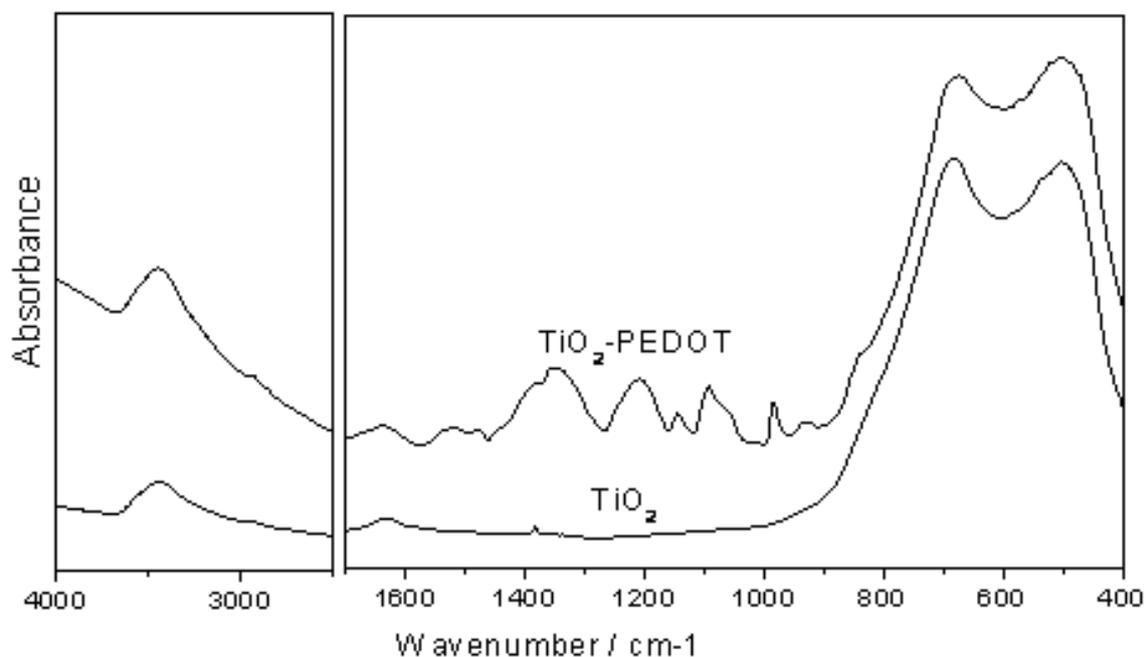


Figure 4. (A) XRD patterns of the electrospun TiO₂ nanofibers and TiO₂-PEDOT nanocables. (B) TGA in the oxygen atmosphere of TiO₂ nanofibers and TiO₂-PEDOT nanocables.

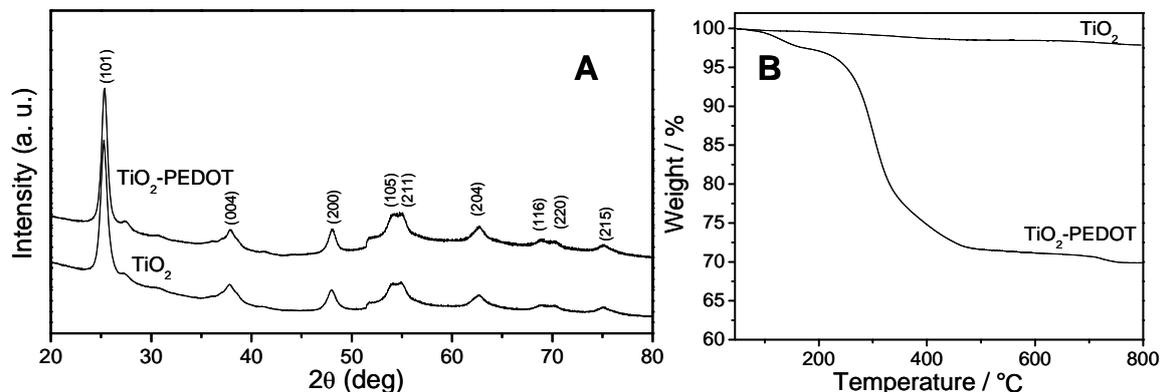


Figure 4A shows the XRD patterns of the TiO₂ nanofibers and the core-sheath TiO₂-PEDOT nanocables. It was found that TiO₂ nanofibers are crystalline and all diffraction peaks can be assigned to the anatase phase of titania, in good agreement with other reports [6,25]. The similar XRD pattern was also obtained for TiO₂-PEDOT nanocables, implying that PEDOT layer is ultra-thin and likely to be in an amorphous state. In order to study the thermal stability of PEDOT coated on TiO₂ template, the thermogravimetric (TG) analysis was also carried out before and after PEDOT-coating and presented in Figure 4B. The TG of TiO₂-PEDOT nanocables shows an initial weight loss of 2.6% is observed up to 180 °C, which may be attributed to the evaporation of the physically adsorbed water and the leaching of the dopant from the polymer composite matrix. The largest weight loss (25.8%) occurs from 180 °C to 505 °C, which is due to the degradation of PEDOT. A total weight loss of 28.4% has been observed up to 800 °C. As a comparison, the thermal behavior of the TiO₂ nanofibers is very stable. There is no significant weight loss observed in the temperature range from room temperature to 800 °C, which is likely due to the highly thermal stability of TiO₂.

2.2. Gas Sensing Performance

TiO₂ nanofibers are very fragile. However, the PEDOT coating on TiO₂ nanofibers enhances the mechanical property of the as-prepared TiO₂-PEDOT nanocables. The TiO₂-PEDOT nanocables possesses an ultra-thin layer of PEDOT, porous mesh structure, and highly specific surface to volume ratio, which favor the adsorption and desorption of gas molecules. In addition, SEM and TEM images show that the ultra-thin PEDOT layer is homogeneous and uniform, thus it can greatly suppress the noises generated from structural defects and then have the potential to improve the limit of detection [3]. Moreover, the PEDOT layer on the TiO₂ nanofibers has a longer conjugation length which can facilitate the charge transport in the TiO₂-PEDOT nanocables [3]. All these features make the as-prepared core-sheath TiO₂-PEDOT nanocables an excellent sensing material.

Figures 5A and 6A represent typical electrical responses of the TiO₂-PEDOT nanocables as a function of time upon periodic exposure to gaseous NO₂ (300 ppb) and NH₃ (10 ppm), respectively. Air was chosen as the carrier gas in both experiments in order to simulate the most common sensing environment. Upon the exposure of TiO₂-PEDOT nanocables to 300 ppb NO₂, the normalized resistance of TiO₂-PEDOT nanocables decreases rapidly by 0.861%. On the contrary, exposure of the

same device to 10 ppm NH_3 efficiently increases the resistance by 0.222%. For three “on-off” cycles of NO_2 or NH_3 , the TiO_2 -PEDOT nanocables show fast, reproducible, and sensitive responses for all three cycles, suggesting that TiO_2 -PEDOT nanocable is a good sensing element in the detection of NO_2 and NH_3 . By purging with dry air, the response of TiO_2 -PEDOT nanocables can be near-completely recovered, indicating the quick desorption of gas molecules from the ultra-thin PEDOT layer and the good reproducibility of TiO_2 -PEDOT nanocables based sensor. The good performance and fast response/recovery can be attributed to the highly porous structure and ultrathin PEDOT-coating layer (~ 6 nm), in which porous structure allows the free access of analyte molecules to PEDOT while ultrathin PEDOT layer greatly reduces the diffusion resistance.

Figure 5. (A) Typical response of TiO_2 -PEDOT nanocables upon periodic exposure of 300 ppb NO_2 . (B) The calibration plot for NO_2 at an applied DC bias of 0.1 V and room temperature.

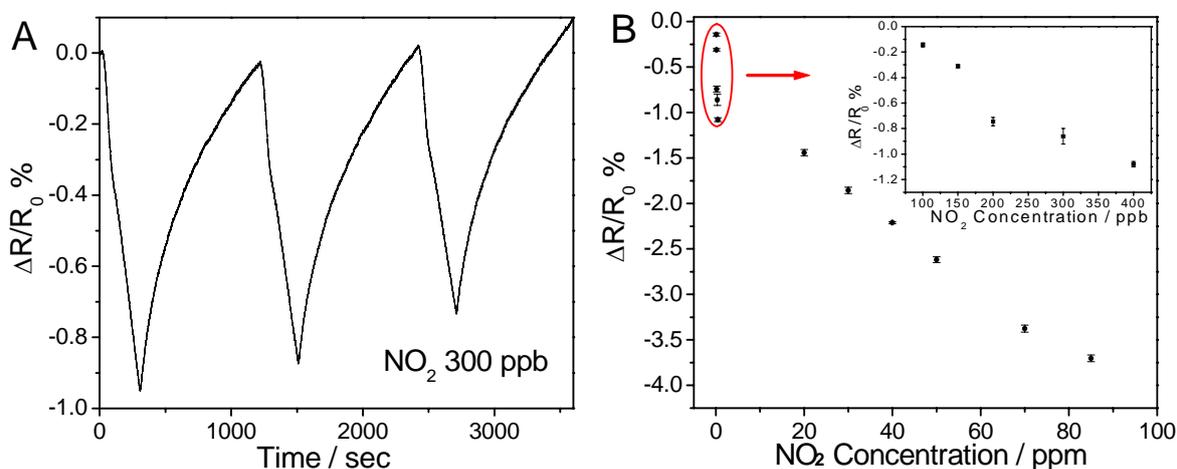
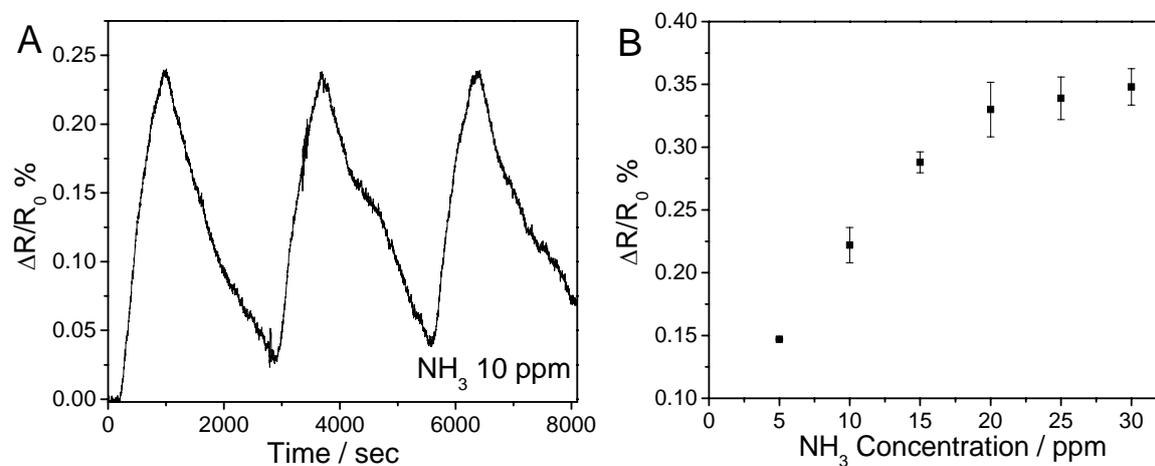


Figure 6. (A) Typical response of TiO_2 -PEDOT nanocables upon periodic exposure of 10 ppm NH_3 . (B) The calibration plot for NH_3 at an applied DC bias of 0.1 V and room temperature.



The gas sensing mechanism of TiO_2 -PEDOT nanocables can be illustrated based on the electrical properties of the sensing element and the chemical property of the analyte molecules. In this study,

FeCl₃ was used as oxidant and the as-prepared PEDOT is *p*-type. NO₂ has an unpaired electron and is known as a strong oxidizer. Upon NO₂ adsorption, charge transfer from PEDOT surface to NO₂ is likely to occur because of the strong electron-withdrawing power of the NO₂ molecules, which might generate more hole-carriers in PEDOT and thus result in the enhanced conductance of PEDOT. In contrast, NH₃ is a Lewis base with a lone electron pair that can be donated to other species. The charge transfer between NH₃ and *p*-type PEDOT leads to the formation of neutral polymer chains and results in the decrease of charge carrier density, which decreases the conductivity of PEDOT.

The response of TiO₂-PEDOT nanocables as a function of NO₂ and NH₃ concentration was presented in Figures 5B and 6B, respectively. For both NO₂ and NH₃, the response of TiO₂-PEDOT nanocables increases with the analyte concentration. At low NO₂ concentrations (<400 ppb), the response of the developed TiO₂-PEDOT nanocables exhibits linear behavior (Figure 5B inset). The normalized resistance change could reach 0.14% upon 100 ppb NO₂ exposure. The detection limit was estimated to be 7 ppb NO₂ at a signal-to-noise ratio of 3, which is lower than EPA current standard of 53 ppb NO₂ for an annual arithmetic mean [34]. However, in the high range of NO₂ concentration (0.4–85 ppm), another linear region was observed with less sensitivity (slope) in Figure 5B. There are only few reports using PEDOT as sensing materials in NO₂ detection. Therefore, these results indicate that core-sheath TiO₂-PEDOT nanocables are promising in sensitive NO₂ detection. On the other hand, the normalized resistance change of TiO₂-PEDOT nanofibers for NH₃ shows a saturation behavior (Figure 6B). One can see that the response initially increases with the concentration of NH₃ and then gradually levels off at a higher concentration. The detection limit was estimated to be 675 ppb NH₃ (S/N = 3), which is significantly lower than the recommended threshold limit value of 25 ppm for human exposure [35] and better than most of reported values based on conducting polymers [19]. It is necessary to point out that the response magnitude of the TiO₂-PEDOT nanocables for the same concentration of NH₃ and/or NO₂ is lower than those of PEDOT Langmuir-Blodgett (LB) film and PEDOT nanorods [15,16], however, the limits of detection for NO₂ and NH₃ achieved in this study is better than most reported values using PEDOT as the sensing element. As the limit of detection is dependent on response magnitude as well as the noise level, such good detection limit obtained in this study may be attributed to ultra-thin, homogeneous and uniform PEDOT layer, which can greatly suppress the noises generated from structural defects and thus improve the limit of detection.

3. Experimental Section

3.1. Materials

3,4-Ethylenedioxythiophene (EDOT), titanium isopropoxide (Ti(OiPr)₄, 97%), and polyvinyl-pyrrolidone (PVP, MW = 1,300,000 g/mol) were obtained from Sigma–Aldrich. Acetic acid (99.8%) and ethanol were bought from Acros Organics and Fisher Scientific, respectively. For gas sensing studies, dry air, nitrogen dioxide (NO₂, 1.036 × 10⁴ ppm and 49.28 ppm in dry air), and ammonia (NH₃, 915.3 ppm in dry air) were purchased from Airgas.

3.2. Fabrication of TiO₂ Nanofibers

TiO₂ nanofibers were prepared by electrospinning using a well-established procedure [25]. Briefly, a 1 mL solution containing 0.1 mL Ti(OiPr)₄, 0.2 mL acetic acid, 0.03g PVP and 0.7 mL ethanol was prepared and electrospun using a 23 gauge needle with a flow rate of 0.3 mL/h at an applied potential of 7 kV and a collection distance of 5 cm. The collected nanofibers were left in air overnight, followed by calcination in a muffle furnace at 500 °C for 3 h to remove PVP and generate TiO₂ nanofibers.

3.3. Synthesis of Conductive Core-sheath TiO₂-PEDOT Nanocables

Vapor deposition polymerization was employed to synthesize the ultra-thin PEDOT coating layer. The collected TiO₂ nanofibers serving as the template for PEDOT coating was carefully dipped into 0.1 mol/L FeCl₃ ethanol solution for 30 min, and then taken out and dried in air for 10 min. After the TiO₂ nanofibers with adsorbed FeCl₃ were exposed to saturated EDOT vapor at 95 °C for 2 days, TiO₂-PEDOT nanocables were produced with TiO₂ as the core and PEDOT as the sheath.

3.4. Characterization of TiO₂ Nanofibers and TiO₂-PEDOT Nanocables

Field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM) were employed to characterize the morphology and the size of the as-prepared TiO₂ nanofibers and TiO₂-PEDOT nanocables. An attached Oxford energy dispersive X-ray (EDX) detector in the FESEM was used for chemical composition analysis. Fourier Transform Infrared (FT-IR) spectra were recorded for KBr disks containing samples with a Nicolet Magna-IR 560 spectrometer. The IR spectra were analyzed using the software of Omnic 7.2a from Thermo Electron Corporation. X-ray diffraction patterns (XRD) were obtained with an Oxford diffraction XcaliburTM PX Ultra with ONYX detector to study the crystal structure of the samples. The thermogravimetry (TG) was performed using a TA instruments (TGA Q500) under an air flow of 60 mL/min and a heating rate of 10 °C/min from room temperature to 800 °C.

3.5. Gas Sensing

A simple TiO₂-PEDOT nanocables-based resistor-type gas sensor was fabricated by placing two electrodes on the as-prepared nanocables with a gap of ~1 mm. Gas sensing experiments were carried out in a homemade 5 cm³ sealed glass chamber with gas inlet and outlet ports. The sensor circuit was subjected to a fixed 0.1 V DC bias and the current was continuously measured by a CHI-601C electrochemical analyzer (CH Instruments Inc., Austin, TX, USA). Dry air was used as carrier gas to obtain the diluted analyte mixture. The mixing of the analyte and carrier gas was regulated by computer-controlled gas mixing system (S-4000, Environics Inc., Tolland, CT, USA). The total flow rate of the gas mixture was set to be 1.2 L/min for NO₂ detection and 0.2 L/min for NH₃ sensing. Prior to the measurement, a stable baseline was obtained by purging dry air through the sensor for one hour, and then NO₂ and NH₃ with various concentrations was introduced to the gas chamber. In a typical NO₂ sensing experiment, the sensor was first exposed to NO₂ (100 ppb to 85 ppm) for 5 min, followed by dry air for 15 min to recover the sensor, and then the procedure was repeated. For NH₃ sensing (5 to 30 ppm), the similar procedure was applied except the exposure and recovery time is 15 min

and 30 min, respectively. The electric resistance of the sensor was calculated by applying Ohm's law ($R = V/I$) while the normalized resistance change is defined as $\Delta R/R_0\% = [(R - R_0) / R_0] \times 100\%$, where R_0 is the initial electrical resistance of the sensor in dry air and R is the measured real-time resistance. All experiments were conducted at ambient temperature.

4. Conclusions

In summary, we have demonstrated a simple and efficient approach to fabricate conductive core-sheath TiO₂-PEDOT nanocables using the as-electrospun TiO₂ nanofibers as template. The as-prepared TiO₂-PEDOT nanocables possess highly porous structure, large surface to volume ratio, and ultra-thin PEDOT layer, providing an excellent material for gas sensing. When used in chemiresistive mode, the TiO₂-PEDOT nanocables exhibited good, reversible, and reproducible concentration-dependent response to gaseous NH₃ and NO₂. The good limit of detection and fast response/recovery can be attributed to background noise reduction and free access of gaseous molecules to ultra-thin PEDOT. This study provides a promising route for the facile and cost-effective synthesis of conductive nanomaterial with ultrathin conducting PEDOT layer.

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