Synthesis of TiO_2/polyaniline core-shell nanofibers and their unique UV photoresponse based on different photoconductive mechanism in oxygen and non-oxygen

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Experiment section

The perparation of TiO_2 nanofibers

2 g of polyvinylpyrrolidone (PVP) was added into the mixed solution composed of tetrabutyl titanate (2 mL) and absolute ethyl alcohol (3.5 mL). Then, 0.5 mL of glacial acetic acid was injected into the mixed solution under stirring until the PVP was dissolved to form blended solutions. The viscous sol of PVP with tetrabutyl titanate composite was contained in a plastic syringe and connected to a high-voltage power supply for electrospinning. An electric potential of 18 kV was applied between the orifice and the ground at a distance of 10 cm. A wire netting substrate (4cm × 4cm) was used for collecting the PVP/tetrabutyl titanate composite nanofibers. After electrospinning of 10 min, the obtained thin sheet of nanofibers was taken down from the wire netting substrate. Finally, the composite nanofibers were calcined at the setting temperature (450 ^oC) at a rate of 5 $^oC/min$ and remained 2 h to obtain pure TiO_2 nanofibers.

The preparation of TiO_2/MnO_2 nanofibers

The electrospun TiO_2 nanofibers sheet was immersed into a 20 mL of glucose (0.3 M) aqueous solution for 15 h. The free space between neighboring nanofibers would allow adsorption of glucose molecules onto the nanofiber surface. Then the sheet of nanofibers was taken out, dried at 50 ^{o}C for 12 h, and further annealed in Ar gas at 500 ^{o}C at a rate of 5 ^{o}C/min and remained 5 h to allow the carbonization of glucose. A thin layer carbon could be painted homogenously on the surface of the TiO_2 nanofibers. To fabricate TiO_2/MnO_2 nanofibers, TiO_2@C nanofibers were immersed into a 10 mL of $KMnO_4$ (0.03 M) aqueous solution and sealed in a Teflon-lined stainless steel autoclave at 160 ^{o}C for 5 h. Due to the interfacial reaction between C and $KMnO_4$, the TiO_2/MnO_2 core-shell nanofibers were obtained. The sheet of TiO_2/MnO_2 core-shell nanofibers was rinsed with distilled water and dried at 50 ^{o}C.

The preparation of TiO_2/PANI nanofibers

TiO_2/MnO_2 core-shell nanofibers was immersed into the 10 mL of HCl (1M) solution. Then 0.2 mL of aniline was added into the above solution. The MnO_2 served as the oxidant for the synthesis of PANI. After reacting for 4-6 h at 0-5 ^{o}C, the dark green sheet of the TiO_2/PANI core-shell nanofibers was taken out and washed with distilled water and absolute ethyl alcohol, then dried at 50 ^{o}C.

Characterization

SEM images were obtained by using a XL-30 ESEM FEG scanning electron microscope operated at 20 KV with gold sputtered on samples. TEM images were obtained using a Philips JEM-2010 transmission electron microscopy at an acceleration voltage of 200 KV. The samples for TEM observation were prepared by dispersing some products in ethanol. This procedure was followed by ultrasonic vibration for 30 min and deposition of a drop of the dispersion onto a carbon-coated copper grid. FT-IR spectrum was measured on an Alpha-Centauri 650 spectrometer with a KBr pellet. The frequency range was 4000-400 cm^{-1}. The XRD was measured with a D/max 2200 PC spectrometer with a Cu Kα source. Scans were made from 3 to 90° (2θ) at the speed of 2° min^{-1}. Electrochemical experiments were all performed with a CHI800B electrochemical workstation in a conventional three-electrode electrochemical cell. An ITO glass (1.5 cm×1 cm) was cut with a nonconducting gap into two pieces and each piece was adopted as an electrode. These dried products were redispersed in ethanol, dropped on the surface of and then dropped on the surface of the gap between the two electrodes to form a thin film, and dried in air at ambient temperature.

All used chemicals were of analytical grade. Aniline (Beijing Chemical Co.) was distilled twice under vacuum before use. HCl was purchased from Beijing chemical factory as the oxidant without further purification. Glacial acetic acid, glucose and $KMnO_4$ were purchased from Beijing chemical factory without further purification. Polyvinylpyrrolidone and tetrabutyl titanate were purchased from Sigma-Aldrich Corporation without further purification.

Our experiment was performed in a big glass container (ca. 30 L). Before the test, the glass container containing the device was filled with oxygen for 20 min in O_2 environment or filled with N_2 for 20 min in non-oxygen environment, respectively.

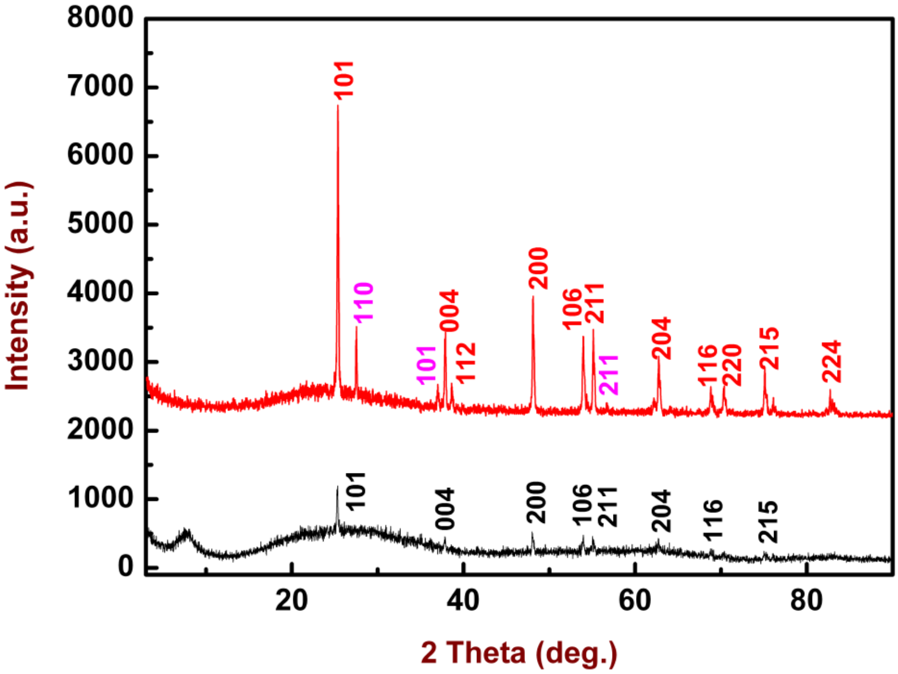

Figure S1 XRD patterns of the TiO_2/PANI nanocomposite (black) and TiO_2/MnO_2 nanocomposite (red).

XRD patterns of the TiO_2/PANI nanocomposite and TiO_2/MnO_2 nanocomposite are shown in Figure S1. In the red line, all the strong sharp diffraction peaks can be indexed as TiO_2/MnO_2 with cell constants of TiO_2 (a=3.782 Å, b=3.782 Å, c=9.503 Å red peak value) and MnO_2 (a=4.404 Å, b=4.404 Å, c=2.876 Å, pink peak value), which are consistent with the values in the literature (JCPDS Card, No. 84-1286 and JCPDS Card, No. 81-2261). XRD pattern of the TiO_2/PANI nanocomposite shows a wide peak around $2\theta=25°$ which is caused by the periodicity perpendicular to the polymer chains of PANI and is indicative of good crystallinity of PANI. A sharp peak at $2\theta=7.53°$ appears, which is close to the PANI repeat distance. This result suggests that PANI has a more ordered structure with relatively distinct Bragg reflections. As shown in Figure (black line), the other strong sharp diffraction peaks can be indexed as TiO_2 with cell constants a=3.782 Å, b=3.782 Å, c=9.503 Å, which are consistent with the values in the literature (JCPDS Card, No. 84-1286). And there is no the peak of MnO_2, which represents the MnO_2 is complete reaction.

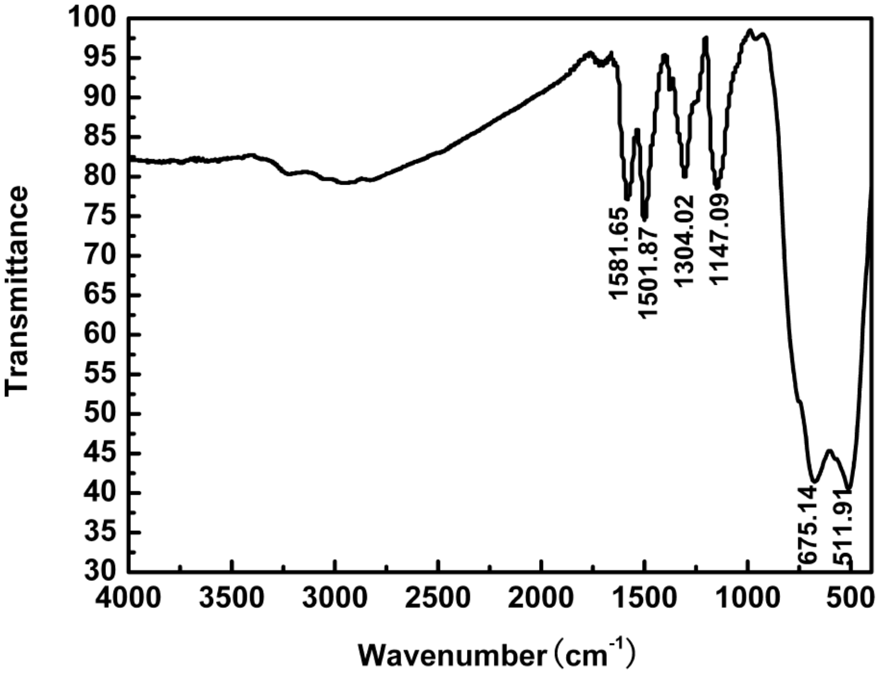

Figure S2 FT-IR spectrum of the TiO_2/PANI core-shell nanofibers.

The well-resolved peaks at 1581 cm^{-1} and 1501 cm^{-1} correspond to the C=C stretching vibration of benzeniod and quinoid rings, respectively. The peak at 1304 cm^{-1} relates to the C-N stretching vibration with aromatic conjugation. The peak at 1147 cm^{-1} assigned to the characteristic of $Q=NH^+-B$ (where Q and B denote quinoid ring and bezene ring, respectively) is also observed. The broad characteristic peak of TiO_2 is found within 400-700 cm^{-1}. The bands at 3360 cm^{-1} can be assigned to stretching vibrations of the –OH group of crystal and adsorbed water molecules. FT-IR spectrum of the TiO_2/PANI nanofibers exhibits characteristic bands of PANI as well as TiO_2, which confirms the presence of both components in the nanofibers.

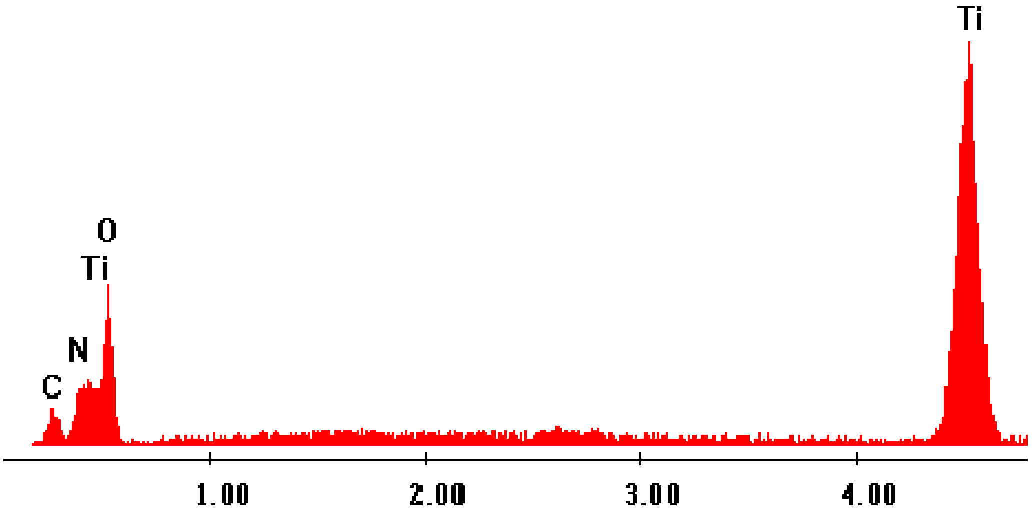

Figure S3 EDX pattern of the TiO_2/PANI core-shell nanofibers.

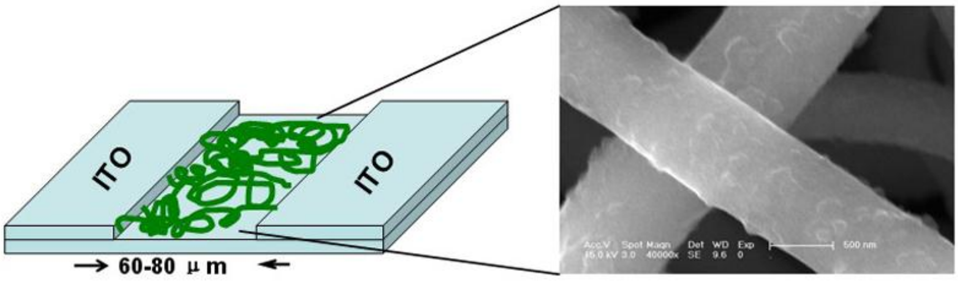

Figure S4 schematic illustration of the device composited with the TiO_2/PANI core-shell nanofibers

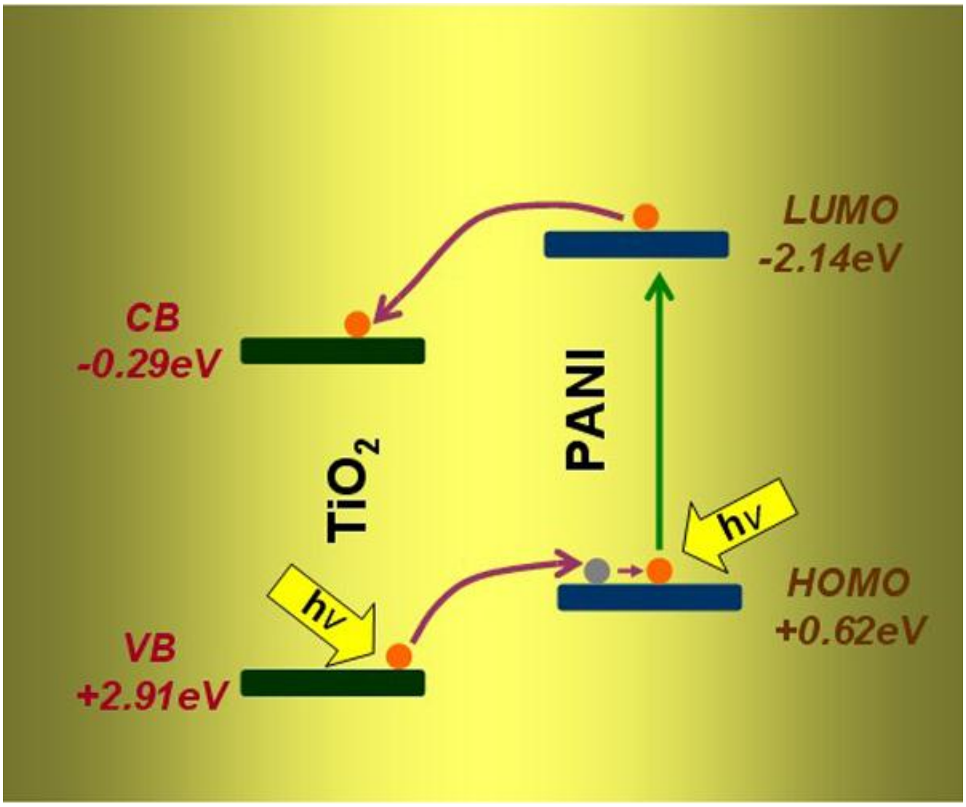

Figure S5 The mechanism of the photocurrent response.