Supporting Information Available:

Manganese Oxide Nanocomposite Fabricated by a Simple Solid-State Reaction and Its Ultraviolet Photoresponse Property

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Synthesis of the PANI functional MnO_2 nanocomposite:

In the typical synthesis, aniline (6.0 mmol) was put into mortar and froze under -20 ^{o}C for 60 min. Then, $KMnO_4$ (3.0 mmol) was added in the mortar, grinding for 30 min. The color of the solid turned from violet to brownish black. After transferred to a beaker, the powder was repeatedly washed with distilled water, ethanol, and acetone until the filtrate was colorless, and then dried under vacuum for 24 h at 40 ^{o}C.

Preparation process of the device containing the MnO_2 nanocomposite:

Electrochemical experiments were all performed in a conventional three-electrode electrochemical cell. An ITO glass was separated with a nonconducting gap into two pieces, and each piece was adopted as an electrode. The gap between the two electrodes is ca. 60-80 µm. The obtained dried products were re-dispersed in ethanol, and then dropped on the surface of the gap between the two electrodes, and dried in air at room temperature, as shown in Fig. S1. In order to prevent interference with visible light and to decrease the thermal effect, the conductivity of the MnO_2 nanocomposite was measured in a dark box at all times, the ultraviolet lamp (365nm) served as light source was 8 W and the distance of the lamp-to-device was greater than 5 cm. A voltage of 1 V is applied across the ITO-ITO electrodes.

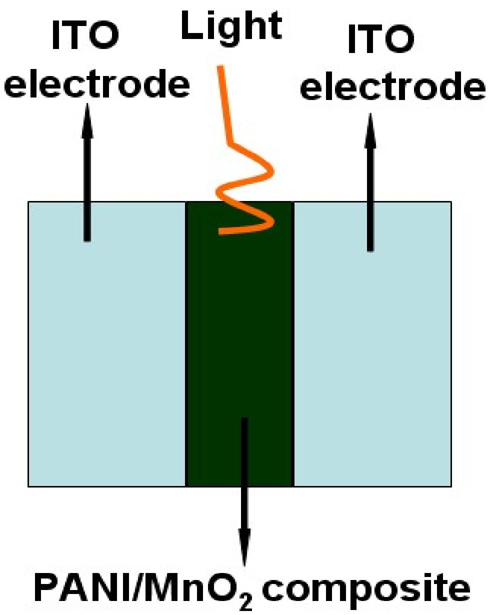

Figure S1 The schematic of the MnO_2 nanocomposites device

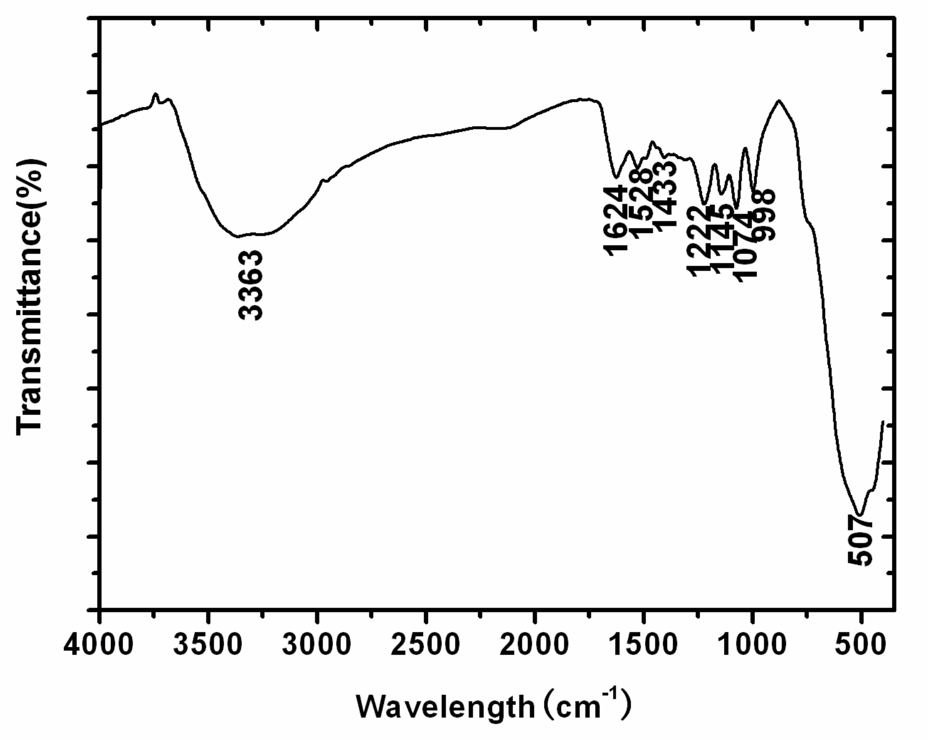

Figure S2 FT-IR spectrum of the PANI functional MnO_2 nanocomposite

The structure of the PANI functional MnO_2 nanocomposite was characterized by FT-IR spectrum. The FT-IR spectrum exhibits the C=C stretching vibration of quinoid ring at 1528 cm^{-1} and benzene ring at 1433 cm^{-1}, the C–N stretching peaks of aromatic amine in the range of 1200–1400 cm^{-1}, the Q=NH^{+}–B absorption peaks (Q: quinoid ring, B: benzene ring) at 1145 cm^{-1}, and the CH_2 bending vibrations in the range from 950 to 1225 cm^{-1}. The peaks at 3363 cm^{-1} and 1624 cm^{-1} can be ascribed to stretching and bending vibrations of the –OH group of water molecules, respectively. The “electron-like peak” at 1145 cm^{-1} suggests that the PANI functionalized MnO_2 nanocomposite has conductivity although no any acidic dopant is added.[1,2] The peak at 507 cm^{-1} relates to Mn–O stretching vibration.

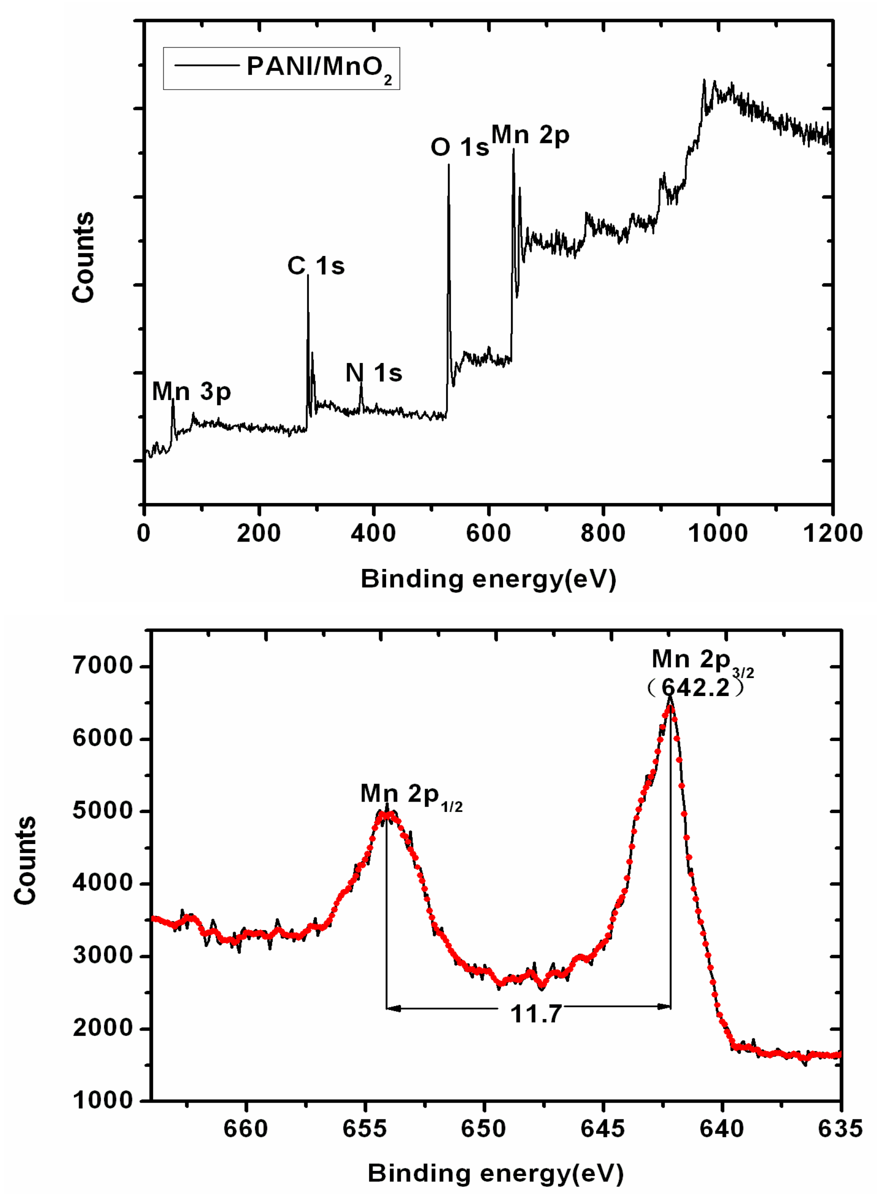

Figure S3 Survey scan and Mn 2p XPS spectrum of the PANI functional MnO_2 nanocomposite

The existence of Mn 3p and Mn 2p signals supplied clear evidence that the obtained nanocomposite contain MnO_2. The Mn 2p region consisted of a spin-orbit doublet with Mn $2p^{1/2}$ having a binding energy of 653.9 eV and Mn $2p^{3/2}$ with a binding energy of 642.2 eV, which is characteristic of a tetravalence manganese system (Mn^{4+}).

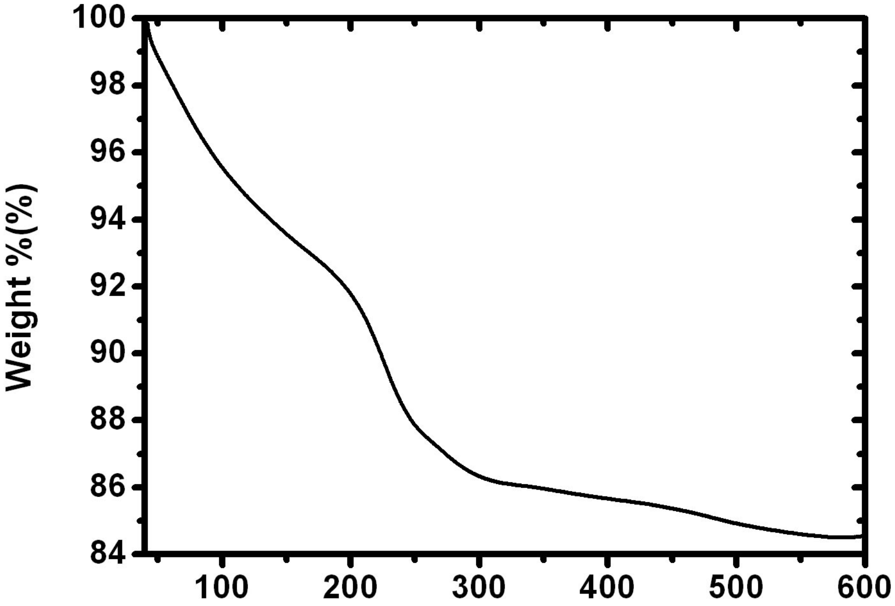

Figure S4 TG curve of the PANI functional MnO_2 nanocomposite

Three major stages of weight loss have been observed. The first loss, located in the range 40–120 °C, was attributed to the evolution of water molecules. The second stage, in the temperature range 120–300 °C, is related to removal of doping anions from the polymer structure. The last weight loss observed between 300 and 600 °C corresponds to the degradation of the polymer chain.[3,4]

The types of measurement apparatus used in this work:

The TEM images were obtained using a Philips JEM-2010 TEM at an acceleration voltage of 200 KV. The samples for TEM observations 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 4000-400cm-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. XPS was performed on an ESCALAB-MKII spectrometer (VG Co., U.K.) with Al Kα X-ray radiation as the X-ray source for excitation. UV-vis absorption spectra of the samples were obtained with Beckman-DU-8B UV spectrophotometer in the range of 200-800 nm. Electrochemical experiments were all performed with a CHI800B electrochemical workstation in a conventional three-electrode electrochemical cell using ITO was cut into two isolated pieces with a sharp knife, and each piece served as an electrode. These dried products were redispersed in ethanol, dropped on the surface of the ITO that existed between the two electrodes, and dried in air. Thermogravimetric analysis(TGA) were carried out using a Shimadzu TGA-50 thermo-gravimetric analyzer at 40–600 ◦C at heating rate 10 ◦C/min in N_2 atmosphere.

References:

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