

Electronic Supplementary Information

Photoelectrochemistry of manganese oxide/mixed phase titanium oxide heterojunction

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Experimental

Materials

All reagents and solvents were purchased from commercial sources and were used without further purification. KF and manganese acetate tetrahydrate were obtained from Merck Company without further purification. Milli-Q water ($18\text{-}20\text{ M}\Omega\cdot\text{cm}^{-1}$ at $27\text{ }^{\circ}\text{C}$) was used for experiments. The electrode materials such as the titanium plate were also obtained from commercial sources. Potassium hydroxide (0.10 M) electrolyte solutions were used for all photoelectrochemical measurements. Before anodization, the titanium plate electrodes were ultrasonically cleaned in distilled water and ethanol, and dried by nitrogen gas flow.

Preparation of Ti-TiO_x (High-voltage) electrodes

The titanium oxide layers on the titanium plate electrodes were prepared according to previously reported high-voltage method⁷⁹. Briefly, the electrodes were immersed in a potassium hydroxide (0.10 M ; $\text{pH} = 13.0$) electrolyte solutions and anodized in a two-electrode system. The titanium plate electrodes, with 1 cm^2 area, were connected to the positive terminal of the potentiostat as working electrode, and a platinum electrode was connected to the negative terminal of a potentiostat as the counter electrode. 50 volts bias potential was applied to the system for 10 minutes . The electrode was washed with distilled water. Then, the obtained electrode was calcined at $550\text{ }^{\circ}\text{C}$ in the air for 12 hours .

Preparation of Ti-nanotube (H₂SO₄/KF) electrodes

Ti-nanotube ($\text{H}_2\text{SO}_4/\text{KF}$) electrodes were prepared according to the reported methods^{34, 81}. Briefly, titanium electrode was immersed in a sulfuric acid (1.0 M) and KF (0.10 M) electrolyte, and anodized in a two-electrode system. The titanium plate electrode was connected to the positive terminal of potentiostat as a working electrode, a platinum-foil electrode was connected to the negative terminal of potentiostat as a counter electrode, and 20 volts bias potential was applied to the

system for 30 minutes. The electrode was washed with distilled water. Then, the prepared electrode was calcined at 550 °C in the air for 12 hours.

Preparation of manganese oxide modified Ti-nanotube (H₂SO₄/KF) and Ti-TiO_x (High-voltage) electrodes

Ti-nanotube (H₂SO₄/KF) and Ti-TiO_x (High-voltage) electrodes were immersed in a 0.1 M sodium acetate aqueous solution containing 0.15 g manganese acetate tetrahydrate. In a three-electrode system, the Ti-nanotube (H₂SO₄/KF) electrodes and Ti-TiO_x (High-voltage) were exposed to the 1.6 V potential versus Ag/AgCl reference electrode for 30 minutes. Afterward, the electrodes were gently washed with distilled water. Then, prepared electrodes were heated at 300 °C in the air for 10 hours.

Photoelectrochemical experiments and data presentation

The photo electrochemical experiments were conducted in a two-electrode system. Although the advantages of three electrode systems for electrochemical and photoelectrochemical studies is well recognized, but considering the fact that there is no reference electrode in actual PEC devices, here in it was preferred not to use reference electrode so the results could be directly applied to PEC devices. In addition to the aforementioned issue, there might be a chance of Cl⁻ leakage from reference electrode, which can preferably oxide on the working electrode which may leads to erroneous conclusions. Moreover, ideally, counter electrode should pass all the current so it can be expected that there is no current passage through reference electrode in order to be sure of its constant potential as reference. However, there always might be a chance of contamination on the surface of counter electrode, which leads to current resistance that cancels out our presumptions.

In photoelectrochemical experiments, to calculate photocurrent, the preferred potential was applied for 3 minutes, and the current was recorded. The electrodes were illuminated for 20 seconds with 2 W LED (wavelength: 410, 460, 530, 580, and 685 nm). The photocurrent obtained by subtraction of the current in the dark (average of recorded current in the dark condition for last 5 seconds before

the start of illumination) from current under illumination (average of recorded current for last 5 seconds before the end of illumination). Schematic presentation of photocurrent data and calculation method is available in electronic supplementary information Fig. S1. It is worth to mention that each experiment results in three photocurrent value which are averaged and reported as final result. Additionally, randomly chosen electrodes were re-prepared and their photoelectrochemical response were reinvestigated in order to assure reproducibility of the results.

UV-DRS spectroscopic experiments and data presentation

UV-DRS spectroscopic data was normalized before presentation. After conversion of reflectance to absorbance ($\text{Absorbance} = 1 - \text{reflectance}$), the normalized absorbance was obtained by dividing the absorbance by maximum value of calculated absorbance for each spectrum. The reason for this normalization is due to solid-state nature of the samples and their different morphologies that leads to different reflection characteristics. Therefore, application ordinary method of a single blank sample for base line correction, which it also has its own reflection characteristic due to its surface morphology, leads to hard to compare and somehow erroneous spectrums.

Characterization

SEM and EDX were carried out with VEGA\TESCAN-XMU. The X-ray powder patterns were recorded by a Bruker D8 ADVANCE diffractometer ($\text{CuK}\alpha$ radiation). Attenuated total reflectance FTIR Spectroscopic measurements were done by Thermo fisher scientific instrument. High-resolution Raman spectroscopy studies were carried out by APUS+ Raman microscope. Photoelectrochemical experiments were conducted in a two-electrode system, in which titanium plate and platinum foil electrodes were used as a working and a counter electrode, respectively. Commercially available 2 Watt LEDs were used as the light sources, and a homemade set up was used as the photoelectrochemical cell.

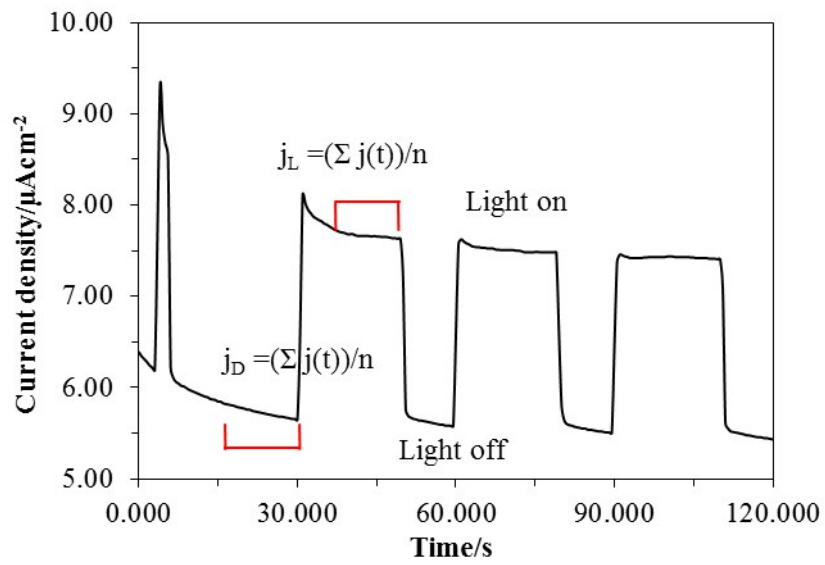


Figure S1. Example plots of photocurrent measurement experiment of pulsed light method in constant potential.

The calculation method used in order to obtain photocurrent is as follows:

$$j_{ph} = j_L - j_D = \Delta j$$

Where j_{ph} is photocurrent amount, j_L is current under illumination, j_D is current in dark and n is number of data points.

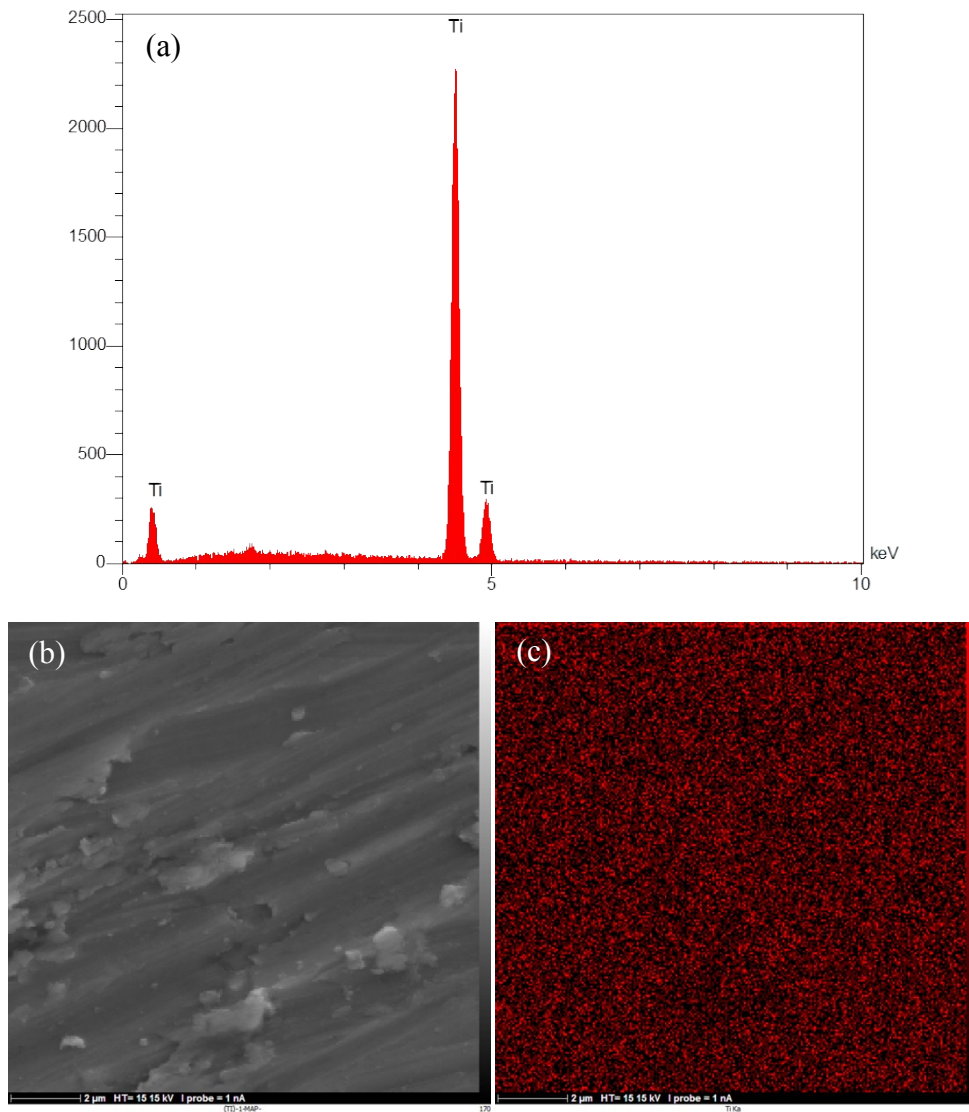


Figure S2. EDX spectra (a), selected area for measurement of EDX map (b) and EDX map (c) of titanium electrode. The red color represents titanium.

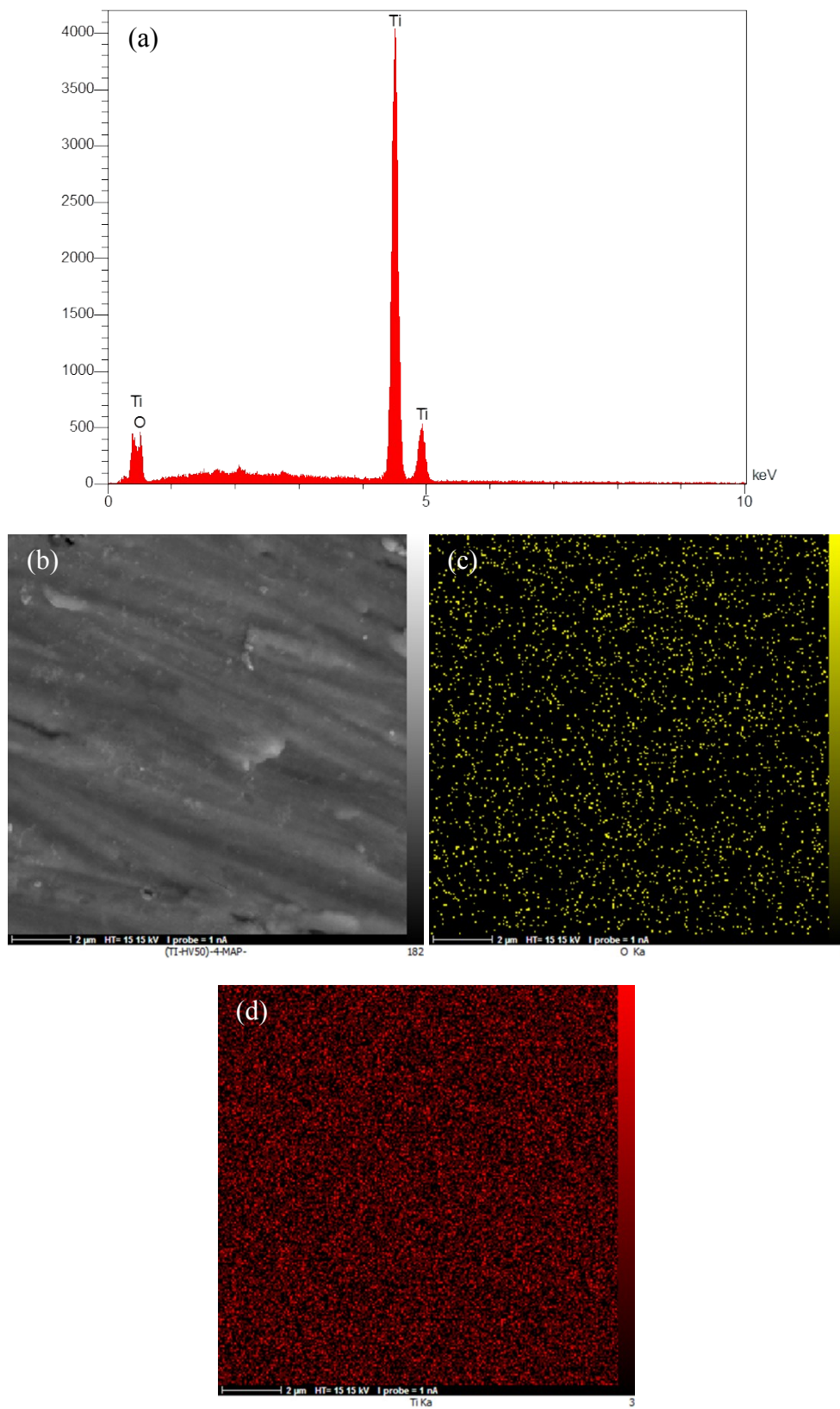


Figure S3. EDX spectra (a), selected area for measurement of EDX map (b) oxygen EDX map (c) and titanium EDX map (d) of Ti-TiO_x (High-voltage) electrode. The red color represents Titanium and the yellow color represents oxygen.

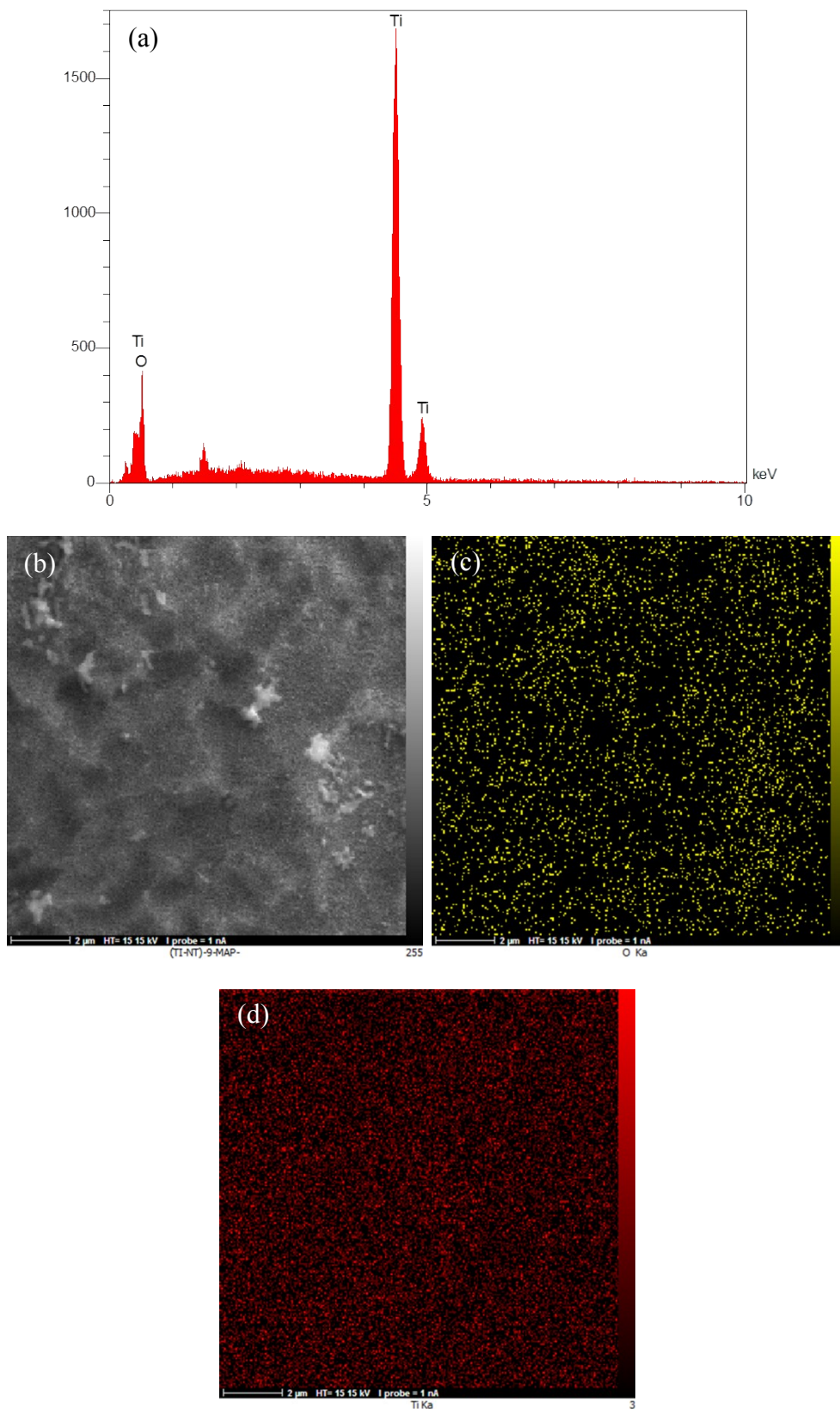


Figure S4. EDX spectra (a), selected area for measurement of EDX map (b) oxygen EDX map (c) and titanium EDX map (d) of TiO_x-nanotube (H₂SO₄/KF) electrode. The red color represents Titanium and the yellow color represents oxygen.

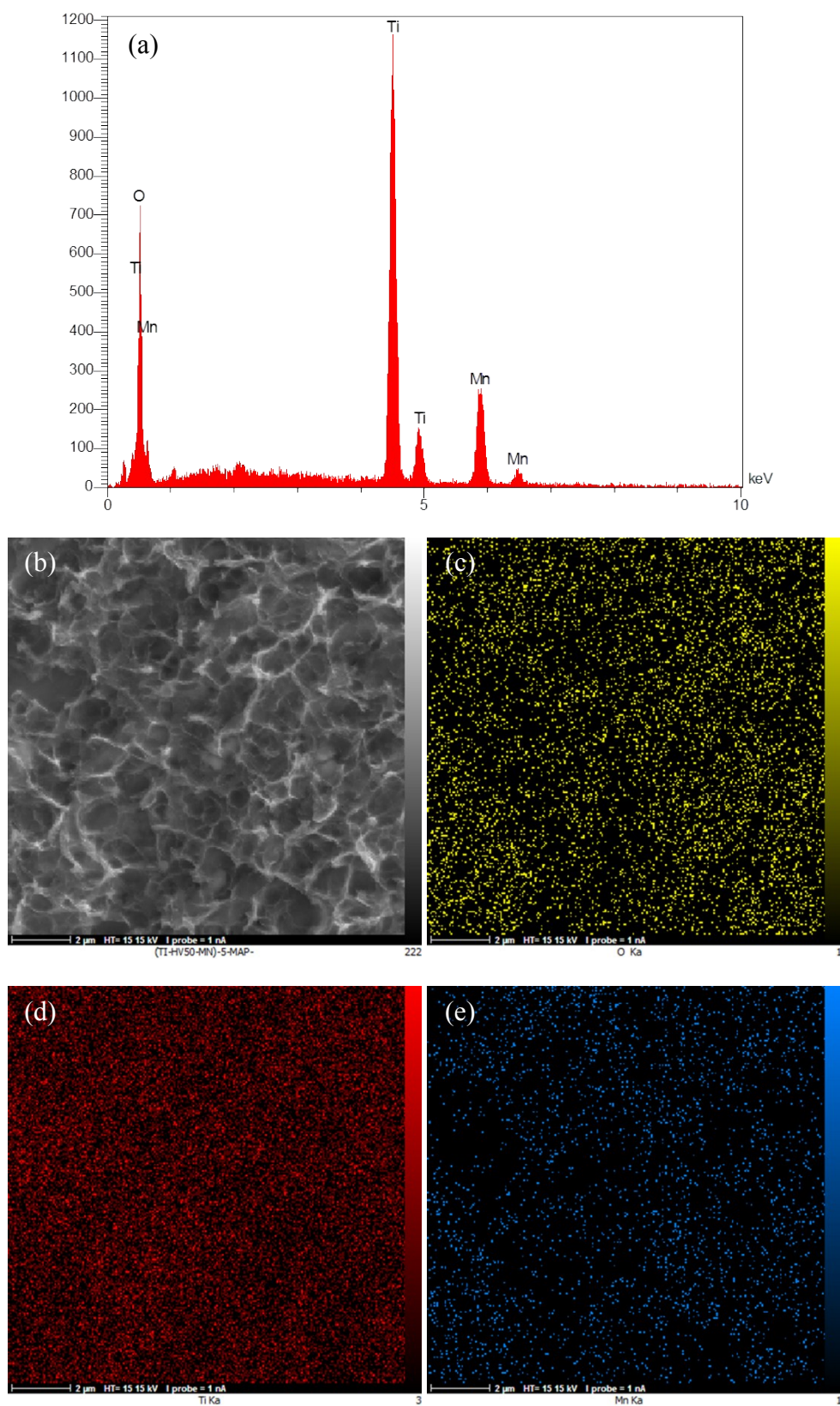


Figure S5. EDX spectra (a), selected area for measurement of EDX map (b) oxygen EDX map (c), titanium EDX map (d) and manganese EDX map (e) of Ti-TiO_x-MnO_x (High-voltage) electrode. The red color represents Titanium, the yellow color represents oxygen and the blue color represents manganese.

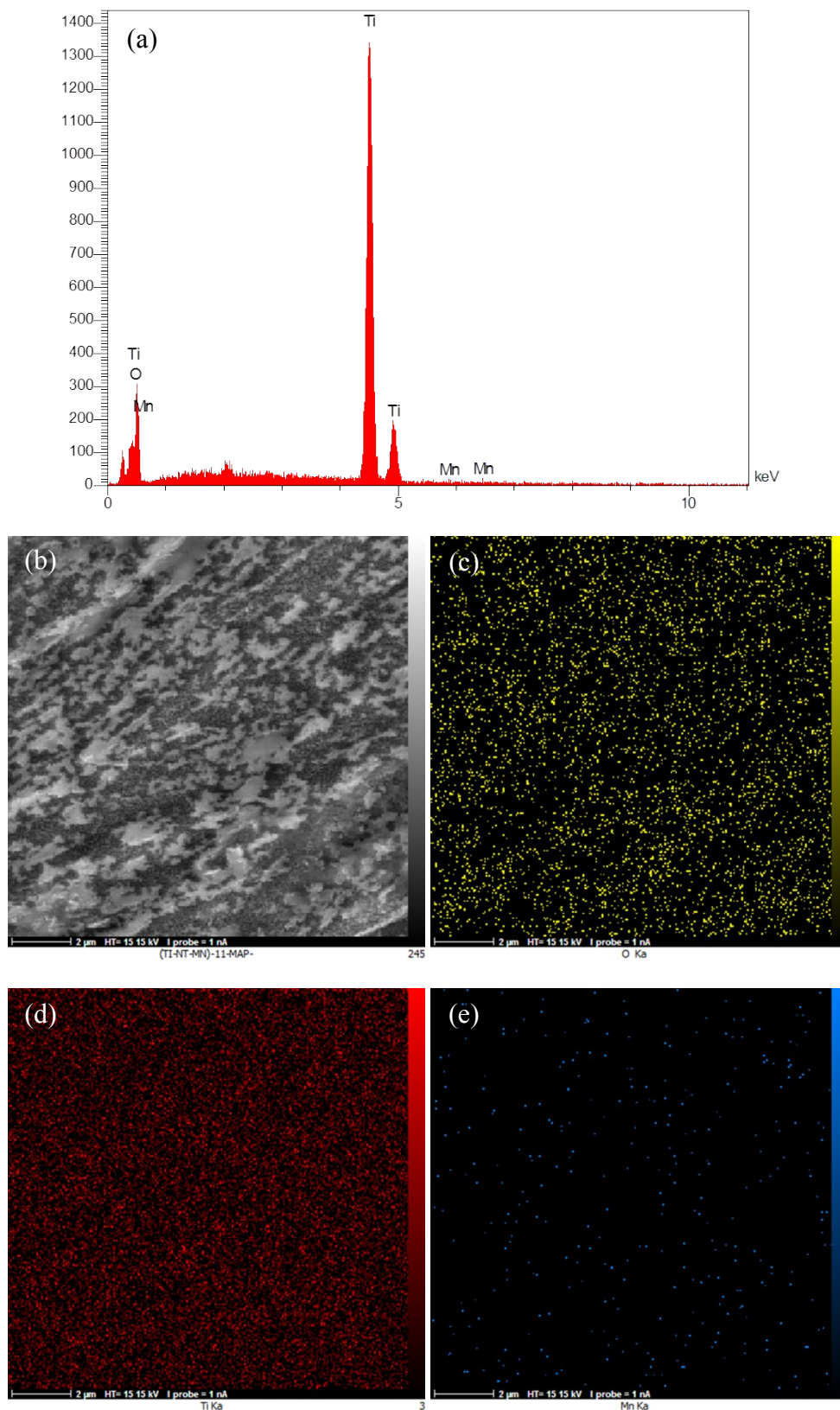


Figure S6. EDX spectra (a), selected area for measurement of EDX map (b) oxygen EDX map (c), titanium EDX map (d) and manganese EDX map (e) of TiO_x-nanotube-MnO_x (H₂SO₄/KF) electrode. The red color represents Titanium, the yellow color represents oxygen and the blue color represents manganese.

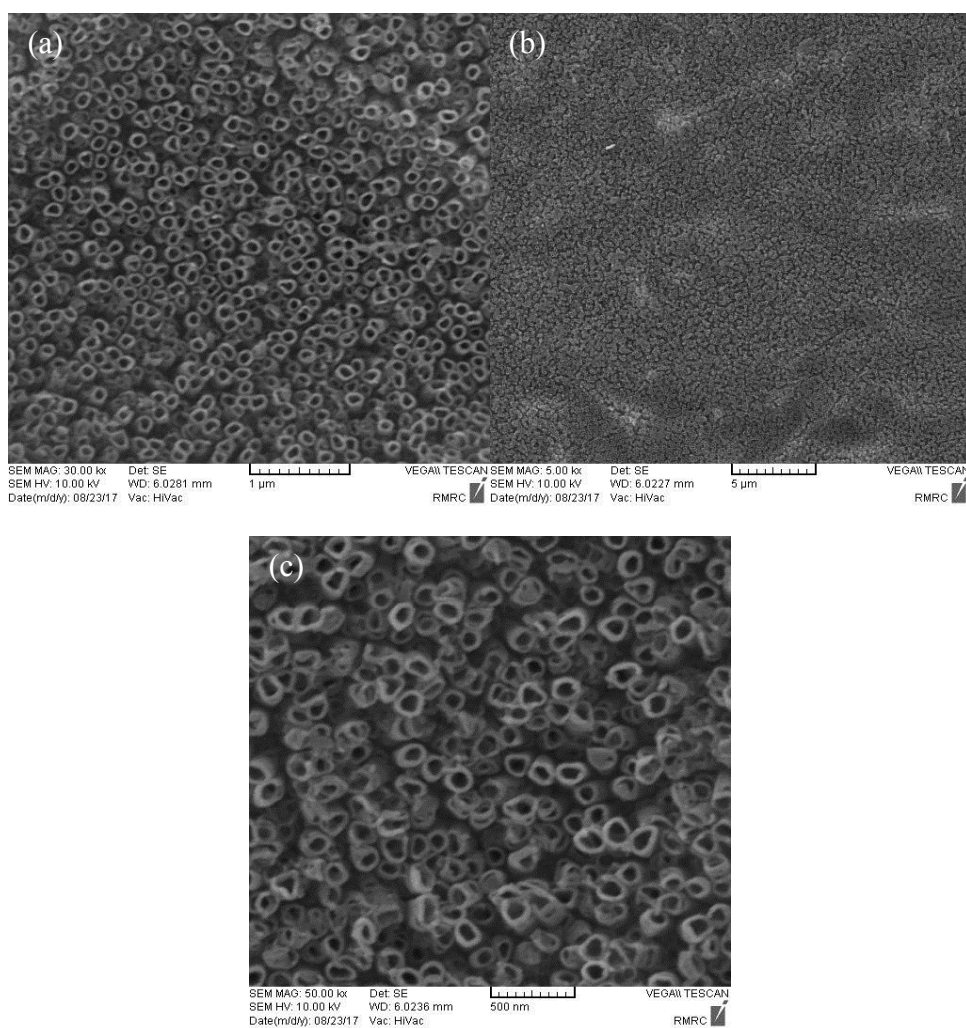


Figure S7. SEM images of TiO_x-nanotube (H₂SO₄/KF) electrode before being calcined in 550 °C for 12 hours with (a) 5 Kx, (b) 30 Kx and (c) 50 Kx magnifications. The electrode prepared in a sulfuric acid (1 M) and KF (0.1 M) electrolyte by anodization at 20 V bias potential versus platinum electrode for 30 minutes.