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Supplementary Information for

Enhancing hot electron collection with nanotube-based three-dimensional catalytic nanodiode under hydrogen oxidation†

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1. Experimental section on the fabrication of TiO_2 nanotube arrays (NTA)

The potentiostatic anodization technique was used to fabricate the TiO_2 NTAs. Titanium thin films were deposited on the SiO_2 substrate by e-beam evaporation using a Ti tablet (99.99% pure) as the Ti source. The SiO_2 substrates were thoroughly cleaned with ethanol and dried under flowing nitrogen gas prior to the titanium deposition. The e-beam evaporator was maintained at a pressure of $2x10^{-6}$ Torr during Ti deposition at a rate of 3 Å/s. Two-step anodization was performed at a potential of 50 V in a typical two-electrode system with the e-beam deposited Ti on SiO_2 as the anode and stainless steel (SUS 316) as the cathode. The electrolyte used during anodization consisted of an ethylene glycol solution with 0.3 weight% of ammonium fluoride and 2 volume% of DI water. The first anodization step was carried out for 5 min; the fabricated nanotubes were then removed by immersing the samples in 1M hydrochloric acid and sonicating for 10 minutes to remove any residual debris on the tubes. Next, a second anodization was conducted on the removed nanotube Ti substrate using the same electrolyte as used for the first anodization. Finally, we obtained well-organized vertical nanotubes with an average length of 700 nm, pore diameter of 70 nm, and a tube wall thickness of 33 nm. The as-synthesized nanotubes are amorphous in nature and highly insulating. To obtain the desired crystallinity, the NTAs were annealed at 450 °C for 2 hours.

2. Experimental section on the fabrication of the Pt/TiO_2 NTA and planar nanodiodes

Pt/TiO_2 NTA catalytic nanodiode fabrication starts with the deposition of 50 nm of Ti onto the SiO_2 substrate and the NTA, which acts as an adhesive layer for the Au on the SiO_2 as well as maintaining an ohmic contact between the NTAs and the gold electrode. 100 nm Au electrodes were then deposited onto the annealed NTA structures as well as onto the SiO_2 substrate. This two-step deposition process of depositing Au/Ti using the same aluminum shadow mask creates the electrode. Finally, a thin layer of Pt either 10 or 30 nm thick was deposited through a second shadow mask onto the NTA structures to connect the Au electrode on the SiO_2, thus forming a Schottky contact between the metal and the semiconductor.

In the case of planar Pt/TiO_2 nanodiode fabrication, 700 nm of Ti was initially deposited on the SiO_2 substrate and annealed in air at 600 °C for 2 hours to convert the titanium to TiO_2. To complete the diode fabrication, we followed a fabrication procedure similar to that discussed above in the NTA-based nanodiode fabrication section for the deposition of the Au electrodes as well as the thin active platinum layer.

3. Experimental section for the measurement of the reaction rate for H_2 oxidation

The H_2 oxidation reaction was performed in a batch reactor (V = 1 L), where the prepared catalyst (10 nm Pt film deposited on the TiO_2 NTA or planar TiO_2) was placed on a standard pyrolytic boron nitride plate heater (Momentive Performance Materials Inc.) in the center of the reactor. After evacuating the chamber up to a base pressure of 3.0×10^{-8} Torr, it was filled with the reacting gas mixture (15 Torr of H_2 and 745 Torr of O_2) at room temperature. The gas mixture was recirculated through the reaction line at a rate of 2 L/min using a metal bellows circulation pump. After equilibrating the gas mixture for 1 hr, we monitored the reaction rate of H_2 oxidation as a function of temperature (50–90 ℃), where the temperature was adjusted using a temperature controller with a K-type thermocouple. To analyze the conversion rate of the chemical reaction, a portion of the gas mixture from the reactor was continuously monitored using a DS iGC 7200 gas chromatograph. The reaction mixture was separated into individual gas species through a 6 ft. long, 1/8'' outer diameter stainless steel 80/100 mesh size column, and the separated gases were detected with a thermal conductivity detector. We calculated the turnover frequency (TOF) based on the product molecules of H_2O produced per metal surface site per second of reaction time. For accurate analysis of the reaction rate, we carried out the reaction in the low conversion regime (< 10 %), where the reaction is kinetically controlled.

4. Active area of the Pt/TiO_2 NTA nanodiode – scanning electron microscopy images

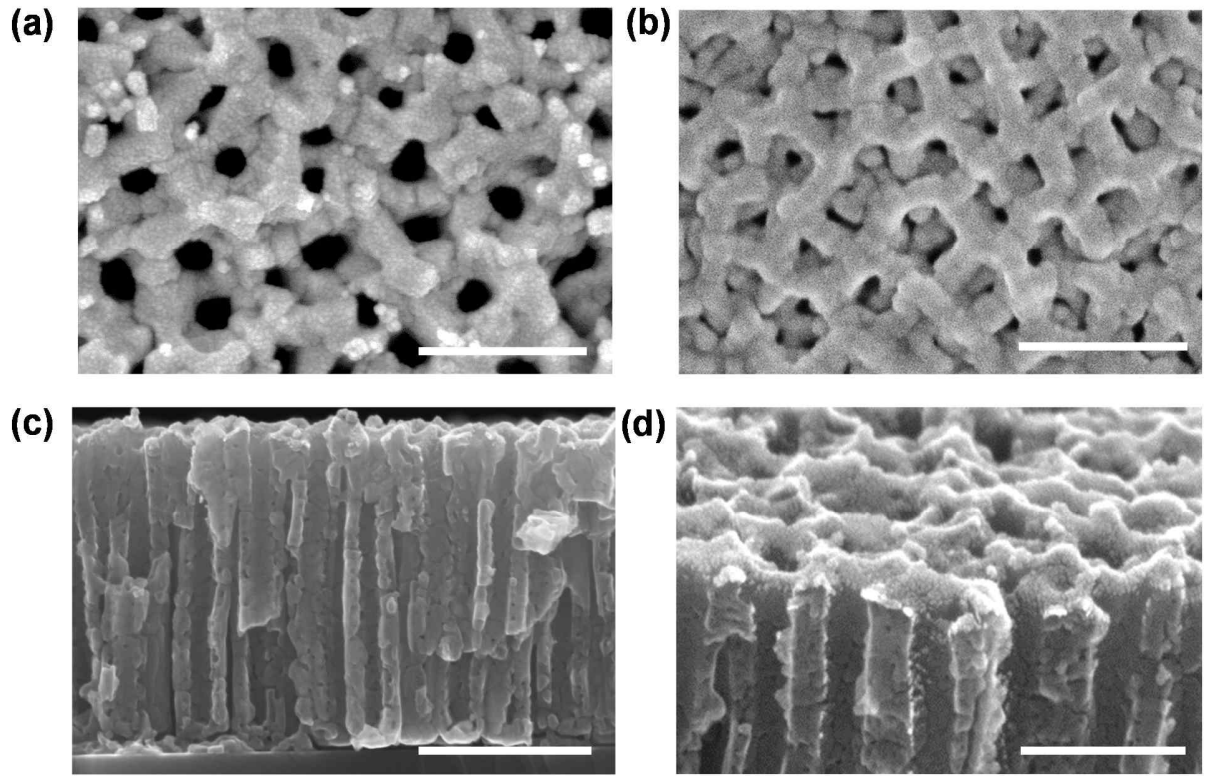

Fig. S1 High-resolution top-view image of (a) the Pt/TiO_2 NTA nanodiode active area with a Pt thickness of 10 nm and (b) the Pt/TiO_2 NTA nanodiode active area with a Pt thickness of 30 nm. (d) Cross-sectional image of the active area constituting the junction of the thin layer of Pt deposited on top of the nanotubes. (d) Magnified image of the Pt/TiO_2 NTA interface at the mouths of the NTA structures. Scale bar: 200 nm

5. I–V characteristics of the Pt/TiO_2 NTA nanodiodes in the H_2 and O_2 gas mixture

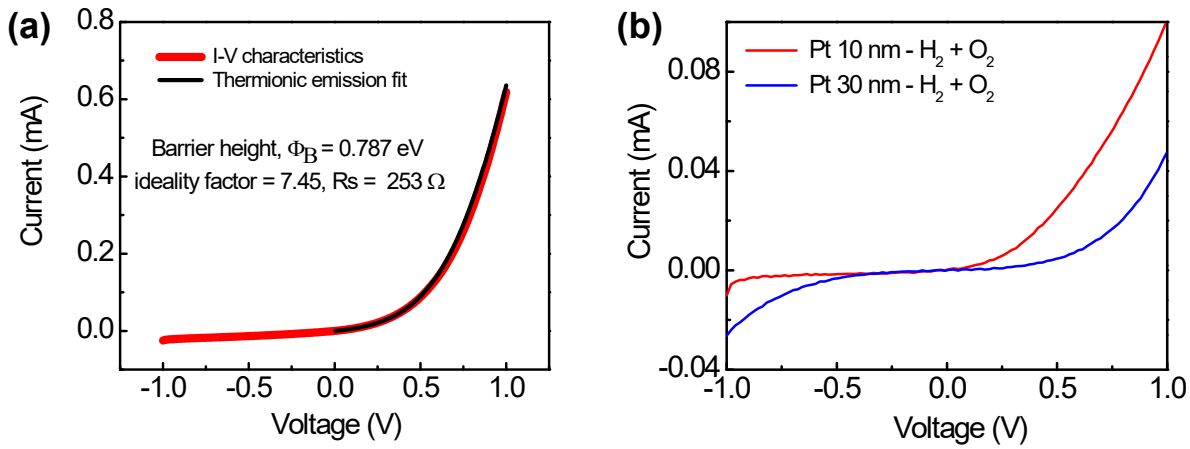

Fig. S2 (a) I–V characteristics of the Pt/TiO_2 NTA nanodiode with the corresponding thermionic emission fitting to determine the Schottky barrier height (Φ_B) and the ideality factor (n). (b) The I–V characteristics of the nanodiodes measured in the H_2 + O_2 gas mixture.

6. I–V characteristics of the planar Pt/TiO_2 nanodiodes in the H_2 and O_2 gas mixture

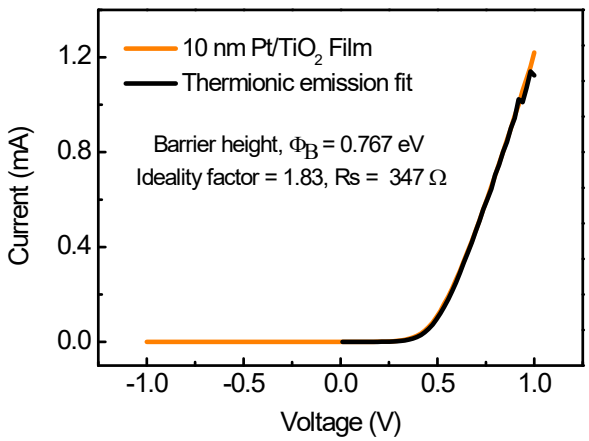

Fig. S3 I–V characteristics of the planar Pt/TiO_2 nanodiode in the gas mixture of H_2 and O_2 with thermionic emission fitting to determine the Schottky barrier height (Φ_B) and the ideality factor (n).

7. Chemicurrent and TOF measured on the planar Pt/TiO_2 nanodiode

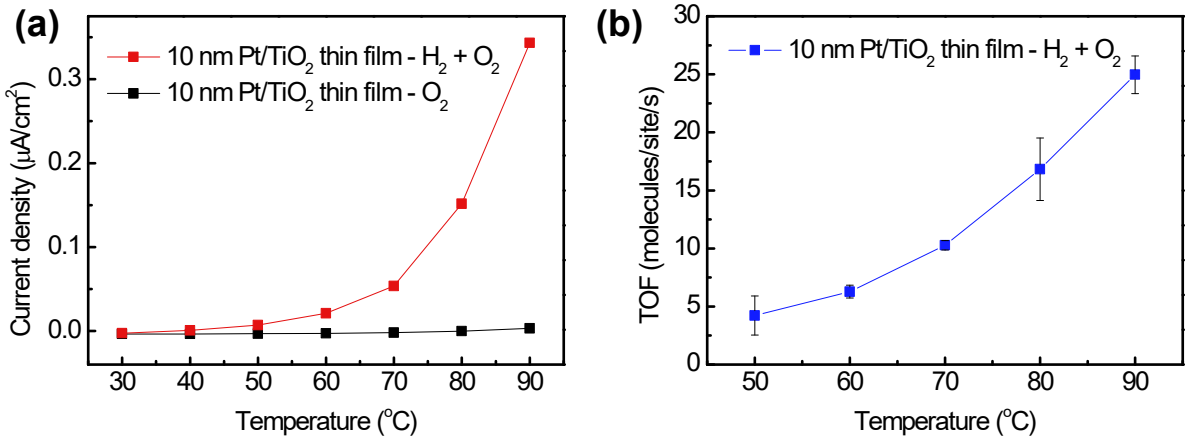

Fig. S4 (a) Temperature-dependent current from the planar Pt/TiO_2 nanodiode with 10 nm Pt measured in the $H_2 + O_2$ gas mixture and in pure O_2. (b) Turnover frequency (TOF) on the Pt deposited TiO_2 film at 50–90 °C.

8. XPS analysis of Pt – before and after the hydrogen oxidation reaction

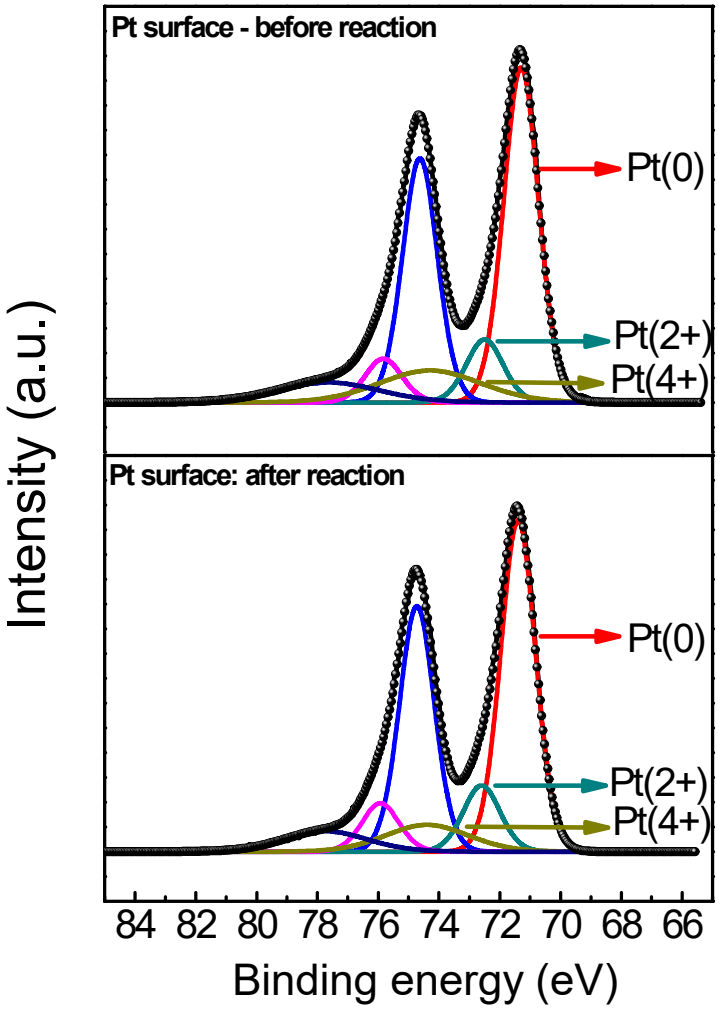

Fig. S5 XPS spectra of the Pt surface on the active area of the Pt/TiO_2 NTA nanodiode, comparing the Pt 4f doublet peaks' binding energies before and after the hydrogen oxidation reaction.