Electronic Supplementary Information

Hematite-based photoelectrochemical platform for visible light-induced biosensing

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Materials and Methods

Materials: Dopamine hydrochloride; Nile Blue A; iron(Ⅲ) chloride hexahydrate; sodium nitrate; β-nicotinamide adenine dinucleotide hydrate (NAD^+); β-nicotinamide adenine dinucleotide, reduced disodium salt hydrate (NADH); urea; glutamate; glucose; lactate; glucose dehydrogenase (GDH); alcohol dehydrogenase (ADH); lactate dehydrogenase (LDH). Human plasma and F-doped tin oxide (FTO)-coated glass slides (surface resistivity ~7 Ω/sq) were purchased from Sigma-Aldrich (USA), while the absolute ethanol was purchased from Merck.

Preparation of PDA-NB-coated hematite: The hematite film was synthesized according to the literatures [17, 18]. FTO-coated glass slides were immersed in an aqueous solution of 0.15 M $FeCl_3 \cdot 6H_2O$ and 1 M $NaNO_3$ and heated at 100°C for 6 hours. After two-step annealing of 550°C for an hour and 15-min short annealing at 800°C, the bright-red film was formed on FTO glass substrates. For PDA-NB coating, 1×2.5 cm substrates (hematite film on FTO glass or glass slides) were immersed into a mixture of dopamine (2 mg/ml) in Tris buffer (pH 8.5) and NB (1 mg/ml) in ethanol for 2 hours. To prevent a leakage of NB, PDA-NB-coated substrates were washed with deionized water for 14 hours. PDA-coated hematite film was fabricated by the same procedure without NB.

Characterization: The morphologies of hematite films were observed using an S-4800 field emission scanning electron microscope (Hitachi High-technologies Co., Japan), and the diffraction pattern of hematite was measured using a D/MAX-RC X-ray diffractometer (Rigaku Co., Japan). The presence of NB was confirmed via UV/Vis absorption spectra using a V-650 spectrophotometer (JASCO Inc., Japan), X-Ray photoelectron spectroscopy (XPS) using a sigma probe spectrometer (Thermo VG Scientific Co., UK), and Raman spectra using a LabRAM HR UV/Vis/NIR High Resolution Micro Raman microscope (Horiba Jobin Yvon, France).

PEC sensing measurements: All the PEC measurements were carried out by a three-electrode system composed of a platinum wire as a counter electrode, Ag/AgCl as a reference electrode (0.197 V vs. SHE), and PDA-NB-coated or PDA-coated hematite film as a working electrode. The working electrode was irradiated by a 450-W Xe lamp with a 420-nm cut-off filter and 50 mM phosphate buffer (pH 7.5) was used as an electrolyte. Linear sweep voltammetry was conducted from -0.4 V to 0.6 V in the absence and presence of 1 mM NADH at a scan rate of 10 mV/s. In photocurrent measurement, the light was switched on and off every 30 seconds under external bias of 0.05 V, and the same potential was applied for selectivity and enzymatic sensing experiments. Enzymatic sensing of glucose, ethanol, and lactate by GDH (326 U), ADH (155 U), and LDH (40 U), respectively, were conducted in a phosphate buffer (pH 7.5) containing 10 mM of NAD^+.

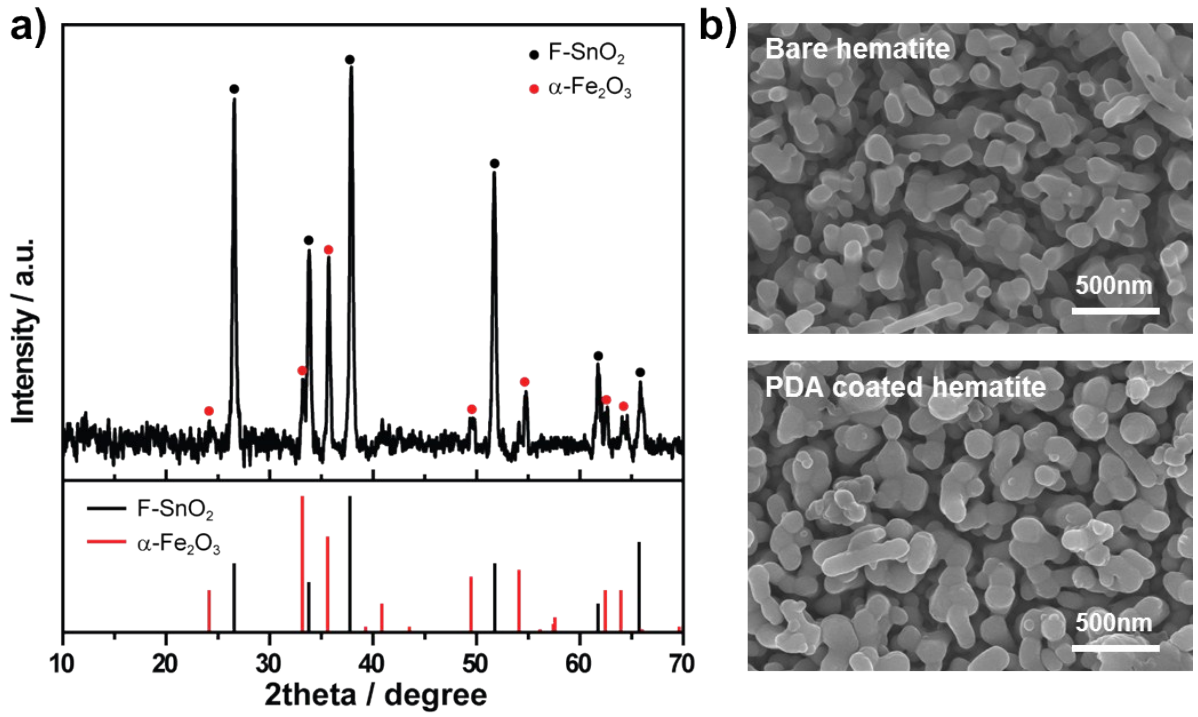

Fig. S1. (a) XRD pattern of hematite film (red circle) on FTO glass (black circle) are well matched with JCPDS #33-0664 (α-Fe_2O_3) and JCPDS #46-1088 (SnO_2). (b) Top-view SEM images of hematite film, showing that it maintains uniform morphology after PDA coating.

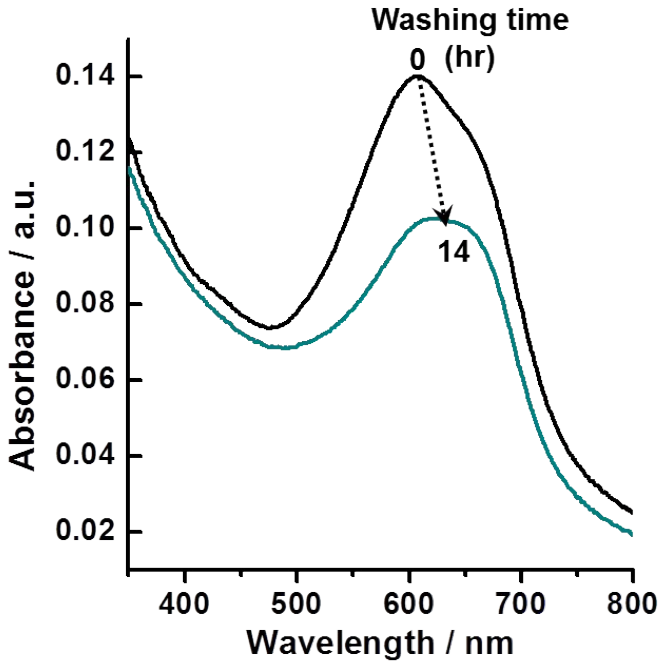

Fig. S2. Absorbance change of PDA-NB-coated glass substrate after 14 hours of washing with deionized water. The leakage of NB induced a decrease in absorbance around 630 nm, but no more leakage occurs after washing. The concentration of NB in the PDA layer was calculated based on absorbance change, showing that approximately 68.7% of NB remained.

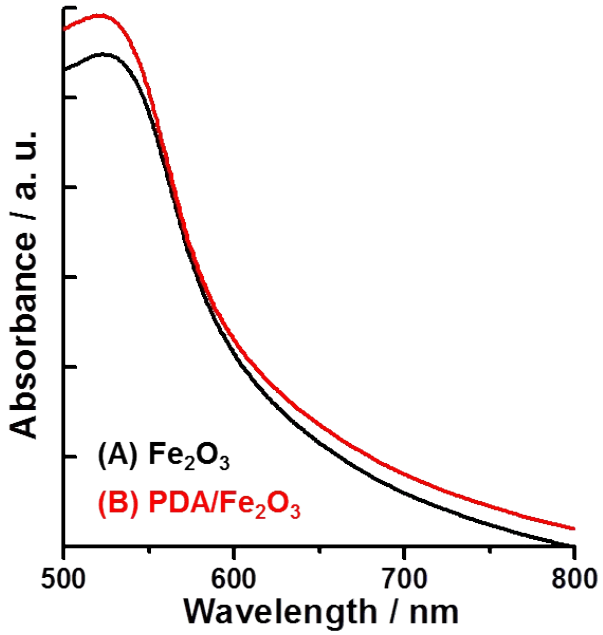

Fig. S3. Absorption spectra of (A) bare Fe_2O_3 and (B) PDA/ Fe_2O_3 films. In contrast to PDA-NB/Fe_2O_3, only a slight increase of absorbance over the entire range of the wavelength was observed due to PDA coating.

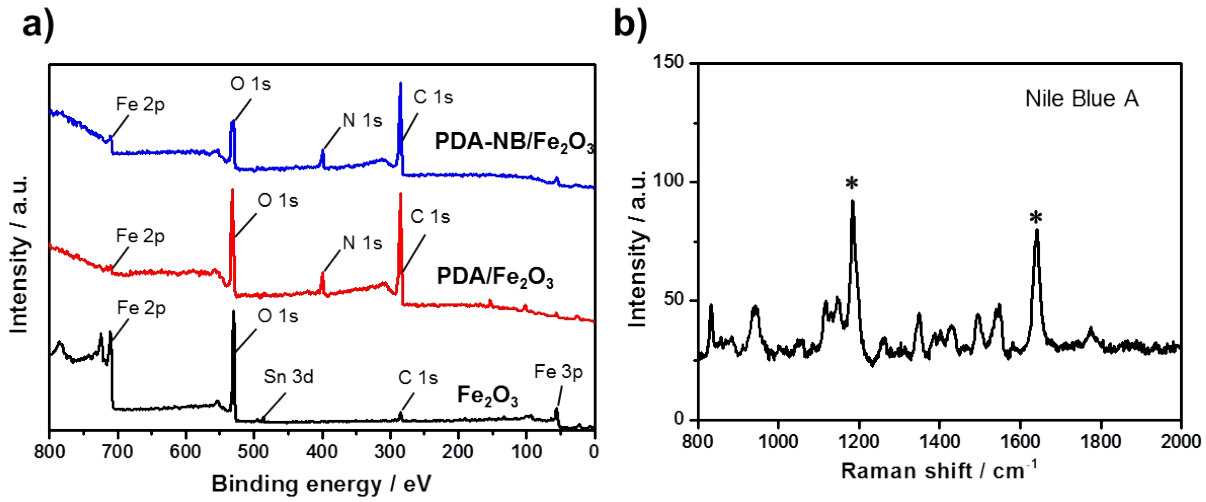

Fig. S4. (a) XPS spectra of Fe_2O_3, PDA/ Fe_2O_3 and PDA-NB/ Fe_2O_3. The Sn3d peak is from the FTO substrate. (b) Raman spectrum of reference Nile Blue A powder. Asterisks indicate the two main peaks of Nile Blue A at 1184 cm^{-1} and 1640 cm^{-1}.

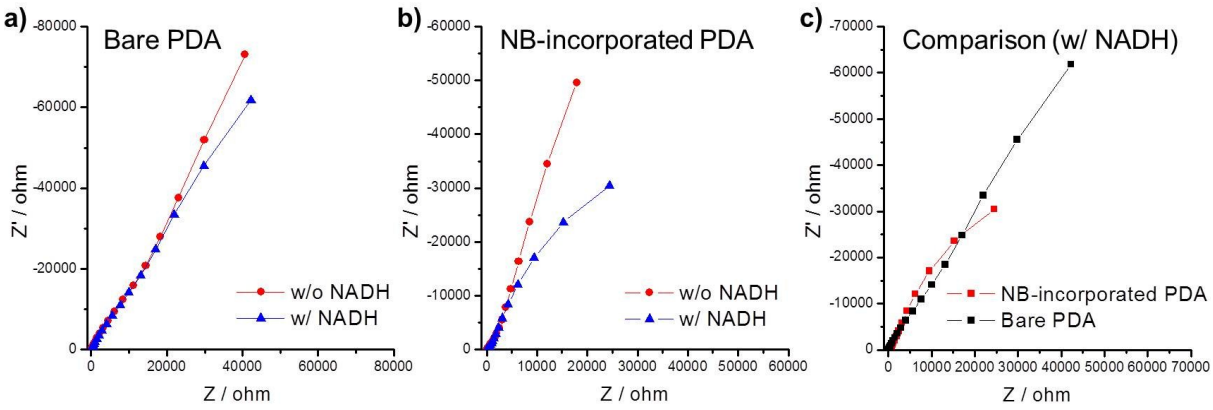

Fig. S5. (a) Nyquist plots of bare PDA, and (b) NB-incorporated PDA with and without NADH in a PB buffer. (c) Comparison of Nyquist plots for bare PDA, and NB-incorporated PDA samples in the NADH solution. The Nyquist plots were obtained in the frequency ranging from 10^5 Hz to 10^{-2} Hz at open circle voltage under visible-light illumination.

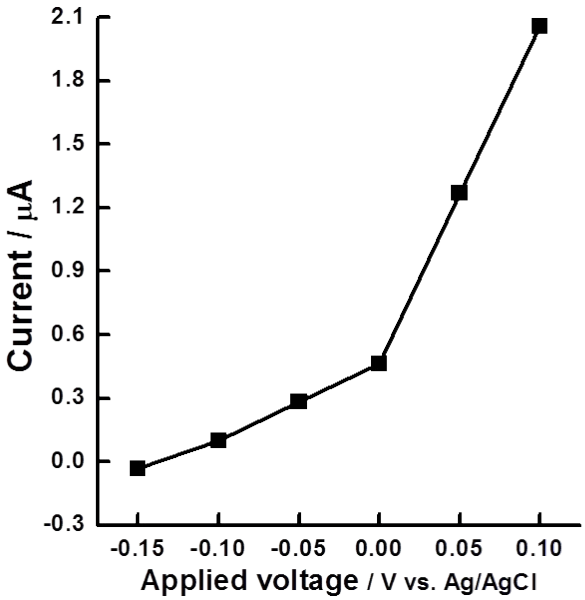

Fig. S6. Photocurrent of PDA-NB/Fe_2O_3 at various applied voltages ranging from -0.15 V to 0.1 V. From -0.15 V to 0 V, the photocurrent increases approximately 3.35 μA/V, while it shows a slope more than four times steeper (16.0 μA/V) over 0 V.

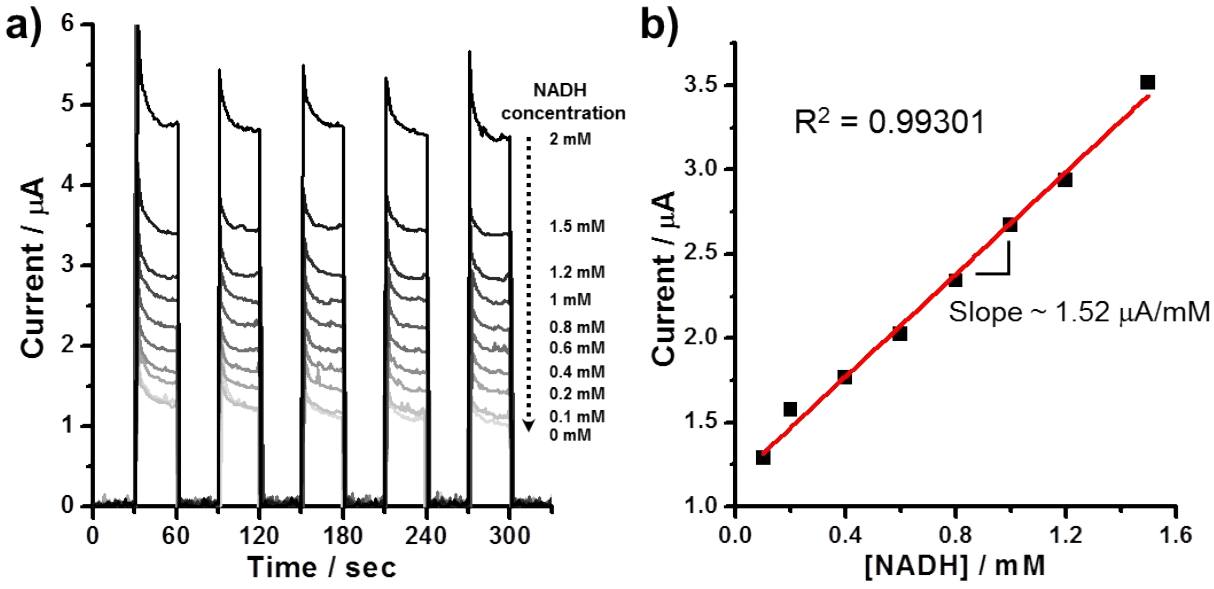

Fig. S7. (a) Photocurrent of PDA/Fe_2O_3 for various NADH concentrations ranging from 0 to 2 mM. (b) Calibration plot of photocurrent versus NADH concentration. PDA/Fe_2O_3 shows poor performance on PEC NADH oxidation with detection limit of 89.8 μM and sensitivity of 1.52 μA/mM.