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Supporting Information

Photoelectrochemical Performance Enhanced by Nickel Oxide-Hematite p-n Junction Photoanode

Jiangtian Li,[a] Fanke Meng,[a] Savan Suri,[a] Weiqiang Ding,[a] Fuqiang Huang[b] and Nianqiang Wu[a,*]

[a]*Department of Mechanical and Aerospace Engineering, West Virginia University, Morgantown, WV 26506-6106, USA.*

[b]*Shanghai Institute of Ceramics, Chinese Academy of Science, Shanghai 200050, China.*

**Corresponding authors: Fax: +1 304 293 6689; Tel: +1 304 293 3326; E-mail: nick.wu@mail.wvu.edu*

Experimental

Synthesis of thin Fe_2O_3 film

The synthesis of thin hematite film was carried out by a drop-coating method.[1] To improve the conductivity of hematite film, 10 mol% Ti was added into the precursor solution. Typically, Titanium butoxide and 70 μL of concentrated HCl were added into 20 ml of 10 mM $FeCl_3$ solution in ethanol. Fluorine-doped tin oxide (FTO) substrates were pre-cleaned with acetone, ethanol and water. The precursor solution was deposited onto the FTO-coated glass by dip-coating, and was subsequently heated in oven at 350 °C for 10 min. This coating-annealing process was repeated for 10 times. The as-prepared films were then further annealed in air at 550 °C for 4 hours.

Deposition of NiO on hematite film

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The deposition of NiO on the hematite film was performed with the similar drop-coating procedure as that of hematite film. The as-prepared hematite film was dipped in 15 mM $Ni(NO_3)_2$ solution in ethanol, and dried at 150 ^oC. Finally, the film was annealed at 550 ^oC for 4h.

Characterization

The surface morphology of hematite films was observed with a JEOL 7600F field-emission scanning electron microscope (FE-SEM) equipped with energy-dispersive X-ray spectroscopy (EDX). Prior to the SEM measurement, gold layer was sputtered on the film for charge compensation. The chemical status of Fe, Ti and Ni was analyzed by X-ray photoelectron spectroscopy (XPS, PHI 5000 Versa Probe system, Physical Electronics, MN). The C 1s peak at 284.8 eV was used as a reference for calibrating the binding energy of all the XPS spectra. The light-absorption properties were characterized by the diffuse reflection mode with Shimadzu 2550 UV-Visible spectrometer equipped with an integrating sphere (UV 2401/2, Shimadzu).

Photoelectrochemical (PEC) tests

The PEC performance was tested with a three-electrode cell using hematite film as the working electrode, Pt wire as the counter electrode, and Ag/AgCl as the reference electrode. 1M NaOH aqueous solution acted as the electrolyte and bubbled for 30 min with N_2 before measurement. The electrochemical data were acquired with Gamry Reference 3000™ Potentiostat/Galvanostat/ZRA Instrument. A 300W of Xe lamp with an AM 1.5G filter was employed as the light source to illuminate the sample. The spectra of incident photo-to-electron conversion efficiency (IPCE) were measured by the same light source and an aligned monochromator (Oriel Cornerstone 130 1/8m). IPCE can be expressed as

$$IPCE = 1240 J / \lambda I_{light} \qquad \text{(S1)}$$

where J is the measured photocurrent density, λ is the wavelength of the incident light, and I_{light} is the measured irradiance at the specific measurement wavelength.

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Mott-Schottky plots

To obtain the Mott-Schottky plots, impedance spectroscopy was performed with a three-electrode cell at AC frequency of 10 kHz in the dark and under the light illumination, respectively. The capacitances were derived from the electrochemical impedance spectra obtained at each potential according to the formula

$$Z_{img}=1/2\pi fC \qquad \text{(S2)}$$

where Z_{img} is the imaginary component of the impedance, f is the frequency and C is the capacitance.[2] The Mott-Schottky plots were then generated with the capacitance values. The slopes determined from the M-S plots were used to estimate the carrier densities according to the following equation. [1]

$$N_d = \left(\frac{2}{e_0 \varepsilon \varepsilon_0}\right)\left[\frac{d\left(\frac{1}{C^2}\right)}{dV}\right]^{-1} \qquad \text{(S3)}$$

where N_d is the donor density (electron donor concentration for an n-type semiconductor or hole acceptor concentration for the p-type semiconductor), C is the capacitance of the space charge region, ε is the dielectric constant of the semiconductor, and ε_0 is the permittivity of free space.

Band alignment measurement

To determine the band level positions and the valence band offset between NiO and Fe_2O_3 p-n junction, X-ray photoelectron spectrometer (XPS) and ultraviolet photoelectron spectrometer (UPS) were carried out with PHI 5000 Versa Probe system to measure the core-levels and valence-band spectra. An UVS 10/35 He lamp at 21.2eV was used as the ultraviolet light source. All the spectra were calibrated by the C 1s peak at 284.8 eV. The details of the method can be found in the literatures.[3,4] The work function was determined by intersection of the secondary electron cutoff occurring at high binding energy. The valence band (VB) energy with respect to the Fermi level (E_f) was extrapolated by the linear portion of the low binding energy side of the proper

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VB peak to the energy axis. [5]

The band offset between the two materials was calculated according to the formula,

$$\Delta E_v = (E_{Ni2p3}^{NiO} - E_{vbm}^{NiO}) - (E_{Fe2p3}^{Fe2O3} - E_{vbm}^{Fe2O3}) + (E_{Fe2p3}^{NiO/Fe2O3} - E_{Ni2p3}^{NiO/Fe2O3}) \quad (S4)$$

Where $(E_{Ni2p3}^{NiO} - E_{vbm}^{NiO})$ is the energy difference between the Ni 2p3 core level and the valence band maximum (VBM) in the NiO film, $(E_{Fe2p3}^{Fe2O3} - E_{vbm}^{Fe2O3})$ is the energy difference between the Fe 2p3 core level and the VBM in the Fe_2O_3 film. $(E_{Fe2p3}^{NiO/Fe2O3} - E_{Ni2p3}^{NiO/Fe2O3})$ is the energy difference between the Fe 2p3 core level and the Ni 2p3 core level in the NiO/Fe_2O_3 p-n junction.

Table 1 lists the peak positions and the VBM positions for all the samples. And the valence band offset was calculated to be 0.21 eV.

Table S1. Peak positions of the core levels (CL) and the valence band maximum (VBM) used for calculation of the valence band offset of the NiO/Hematite p-n junction.

Samples	Region	Binding Energy (eV)
n-Fe_2O_3	Fe 2p3	709.88
	VBM	1.4
p-NiO	Ni 2p3	853.94
	VBM	0.45
p-NiO/n-Fe_2O_3	Fe 2p3	709.69
	Ni 2p3	854.49

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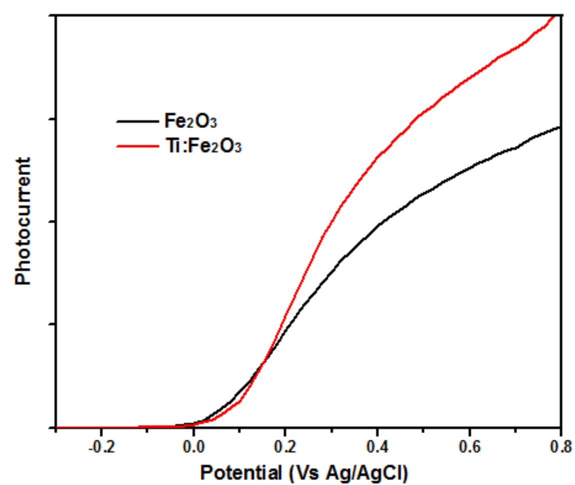

Figure S1. Photocurrent densities of the Ti doped and the undoped hematite films.

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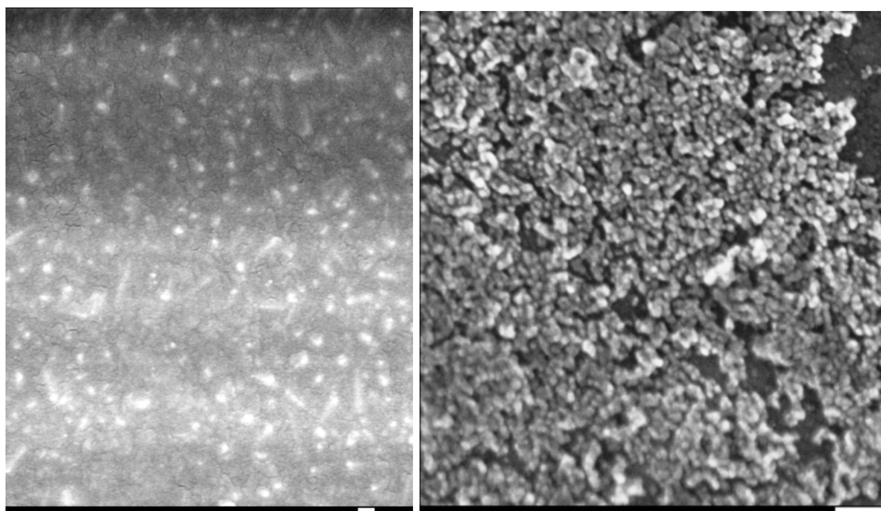

Figure S2. SEM images of the NiO/hematite films after one cycle (Left) and six cycles (Right) of NiO deposition. On the surface of hematite, some white points were observed (Left image), which was attributed to the deposition of NiO nanoparticles. The NiO nanoparticles contacted tightly with hematite to form the p-n junction. After six cycles of deposition, a thin NiO particle layer with an almost full coverage was obtained (Right image). The scale bar is 100 nm in both the images.

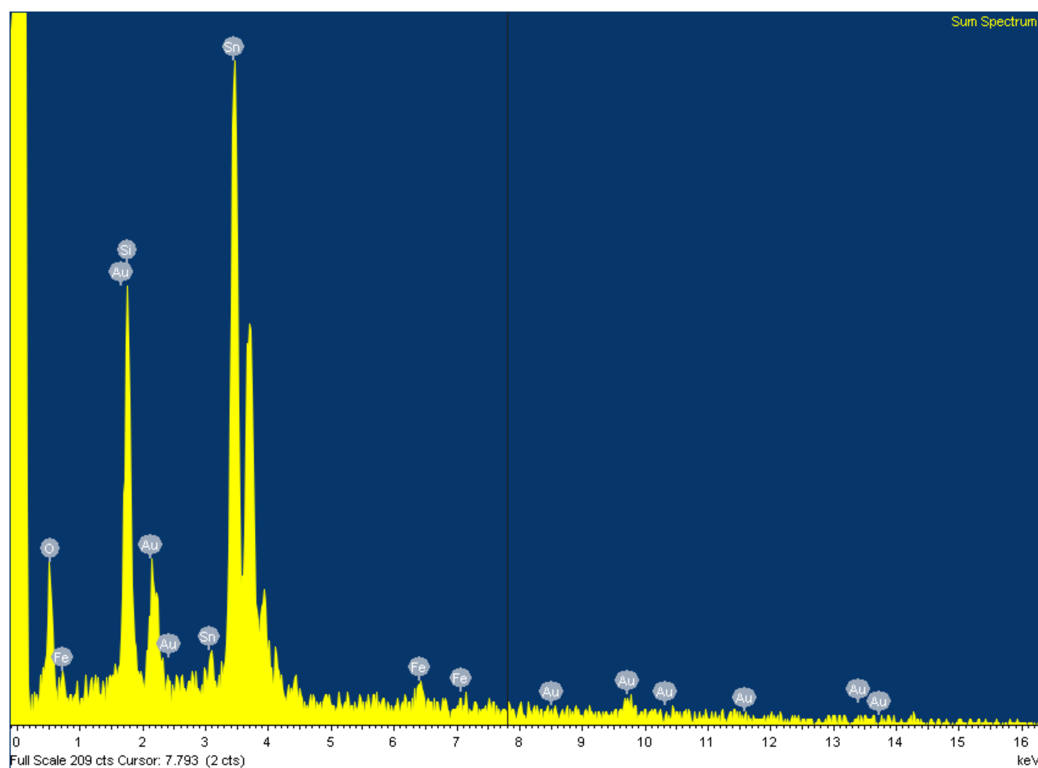

Figure S3. Typical EDX spectrum obtained from the NiO/Hematite photodiode film. It can be seen that the Fe peak was very weak and no Ni peak can be detected. Sn came from the FTO substrate, and Au came from the deposited Au layer to reduce the charging of hematite.

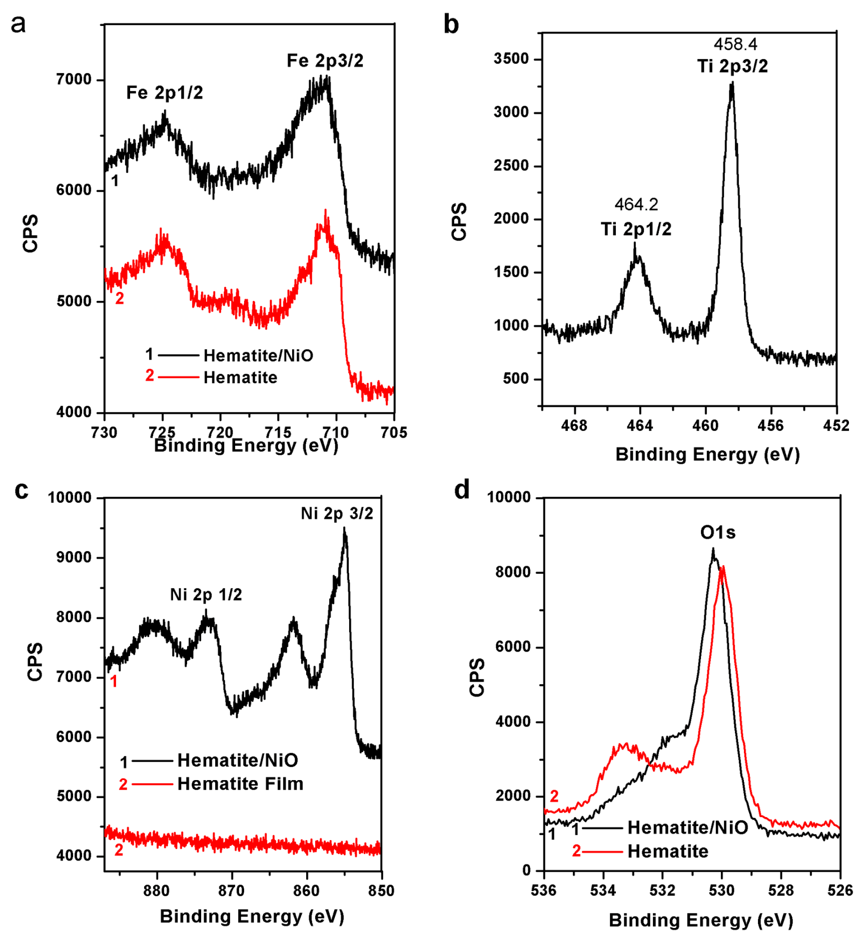

Figure **S4**. XPS spectra for Fe (*a*), Ti (*b*), Ni (*c*) and O (*d*) of the hematite film and the NiO/hematite film, respectively.

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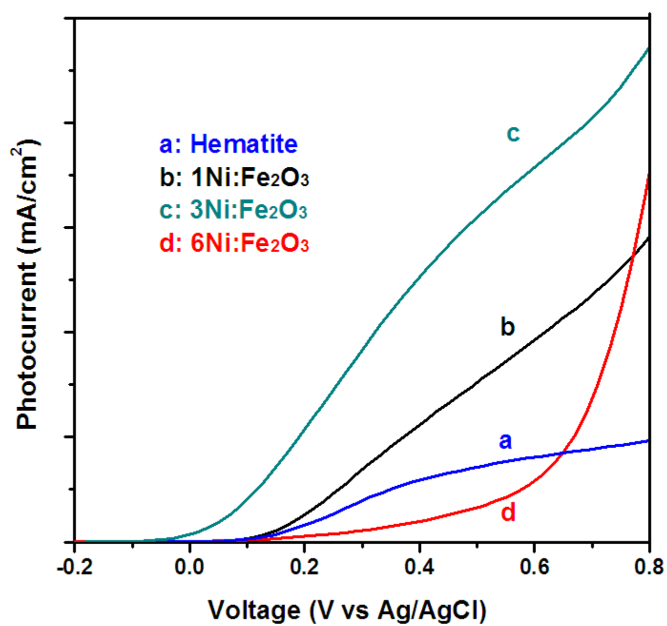

Figure S5. Photocurrent density of the NiO/hematite photodiode films as a function of the NiO deposition cycle.