Supporting Information

Solar Driven Hydrogen Releasing from Urea and Human Urine

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Experimental section

Synthesis of TiO_2 nanowire arrays

TiO_2 nanowire arrays were synthesized on a FTO glass substrate by a hydrothermal method reported elsewhere.[1] A Ti precursor solution was prepared by mixing 15 ml concentrated HCl (36.5%) with 15 ml deionized water, and follow by the addition of 0.5 ml titanium n-butoxide. A piece of FTO substrate was cleaned with acetone, ethanol and then water. The substrate was transferred into a Teflon lined autoclaves, with the substrate against the inner wall of the autoclave, and then filled with Ti precursor solution. The sealed autoclave was heated at 150 ^{o}C in an electric oven for 5h. After the autoclave cooled down, FTO substrate was coated with a uniform white film of TiO_2 nanowire arrays.

The as-prepared TiO_2 nanowires were annealed in air at 550 ^{o}C for 3h. The air-annealed TiO_2 nanowires were further annealed in hydrogen atmosphere at 350 ^{o}C for additional 30 min in a home-built tube furnace system filled with ultrahigh purity hydrogen gas (99.999%, Praxair). The white TiO_2 nanowire film turns into pale yellow in color after hydrogen treatment.

Synthesis of α-Fe_2O_3 nanowire arrays

Hematite (α-Fe_2O_3) nanowire arrays were synthesized by a hydrothermal method described elsewhere. [2] A piece of pre-cleaned FTO substrate was put into an autoclave filled with a 20 ml precursor solution mixed with 0.15 M ferric chloride and 1 M sodium nitrate solution. The pH of the precursor solution was adjusted to be 1.5 by HCl solution. The sealed autoclave was heated at 95 ^{o}C for 4h. After the autoclave cooled down, FTO substrate was coated with a uniform yellow film of β-FeOOH nanowire arrays.

The β-FeOOH nanowire film was further annealed in N_2-air mixture at 550 °C for 2 hr at 740 Torr pressure with a N_2 flow rate of 50 sccm. The tube furnace was first vacuumed to a pressure of 15 Torr, and then filled with ultrahigh purity N_2 (99.998%, Praxair). The initial oxygen content was estimated to be 0.43 % ($O_2/(O_2+N_2)$, volume %).

Deposition of $Ni(OH)_2$ (urea oxidation catalyst)

$Ni(OH)_2$ was deposited onto α-Fe_2O_3 and TiO_2 nanowire arrays by successive dip-coating method. 0.1 M $Ni(NO_3)_2$ aqueous solution and 1 M NaOH solution were prepared. Nanowire-arrayed electrodes were dipped into $Ni(NO_3)_2$ solution for 10 s, then blown dry with compressed air. Then the electrodes were dipped into NaOH solution for another 10 s, and blown dry with compressed air. This process is considered as one dip-coating cycle. The deposition of $Ni(OH)_2$ was repeated for 3 dip-coating cycles.

Material Characterization

X-ray diffraction (XRD) spectra of TiO_2 and α-Fe_2O_3 were collected on a Rigaku Americas Miniflex Plus powder diffractometer. Scanning electron microscopy (SEM) images and energy dispersive X-ray spectroscopy (EDS) spectra were collected with a field emission SEM (Hitachi S-4800II). Electrochemical and photoelectrochemical measurements were collected using an electrochemical workstation CHI 660D coupled with a 150 W xenon lamp (Newport 6255) with an AM 1.5 global filter (Newport 81094). The urea electrolyte was 0.33 M urea in 1.0 M NaOH aqueous solution. Real urine was obtained from a healthy male adult (age: 26). The urine electrolyte was human urine solution mixed with a 1.0 M NaOH solution. Ag/AgCl and a Pt wire were used as reference and counter electrode, respectively. The gas produced on the Pt counter electrode was collected by a 1-mL syringe. The composition of the produced gas was analyzed by a gas chromatography (Agilent 3000).

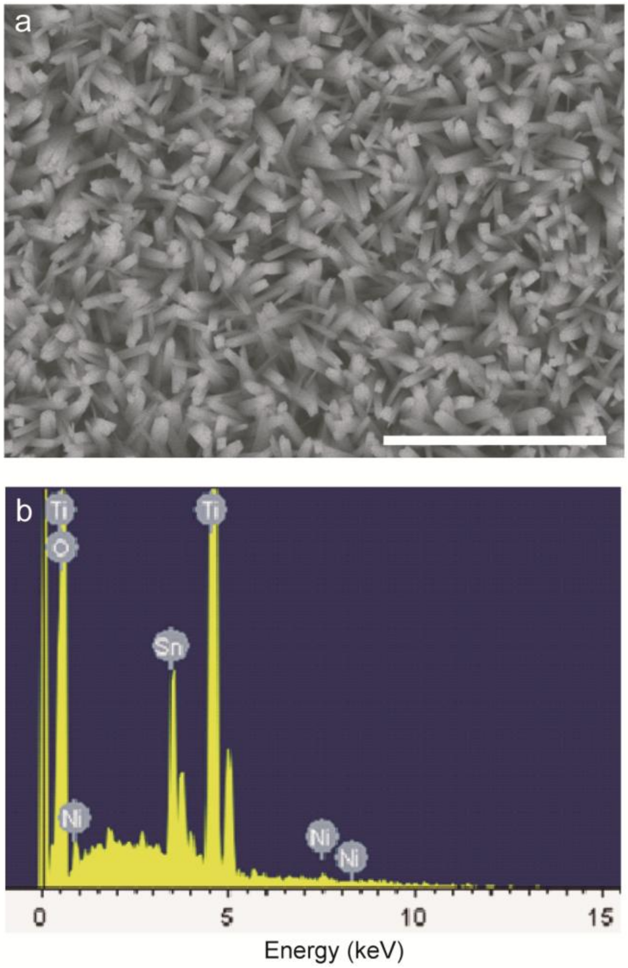

Figure S-1. (a) SEM image of $Ni(OH)_2$ modified TiO_2 nanowire arrays. Scale bar: 2 μm. (b) EDS spectrum collected from Ni-TiO_2 nanowires grown on FTO substrate.

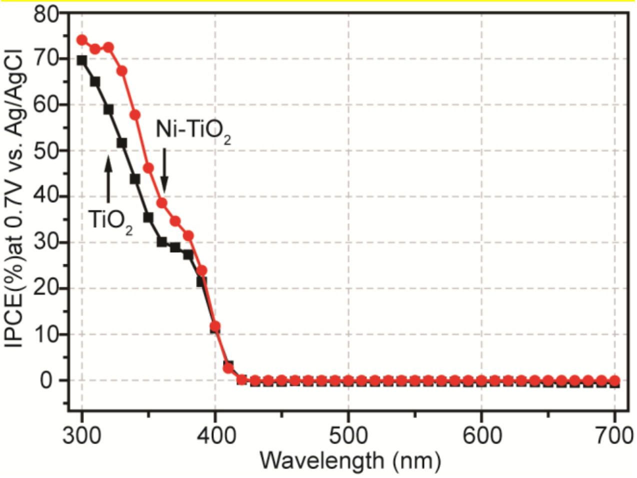

Figure S-2. IPCE spectra collected for TiO_2 and Ni-TiO_2 electrodes at -0.7 V vs. Ag/AgCl.

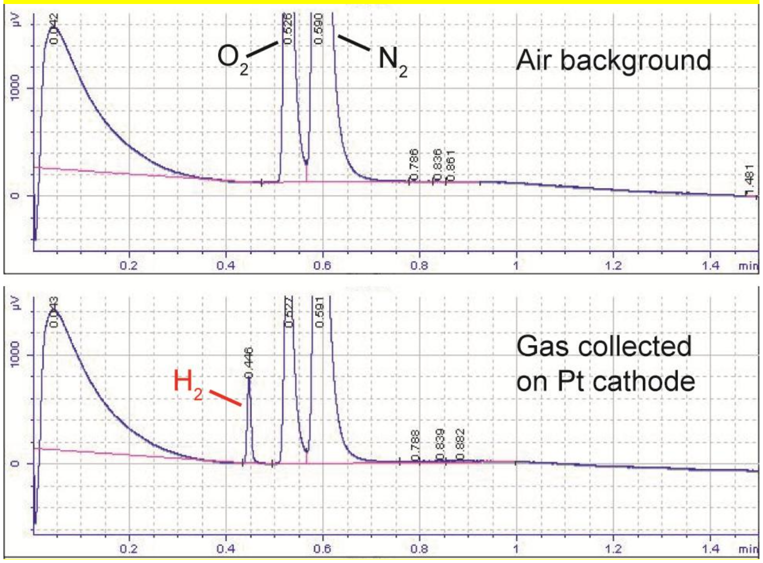

Figure S-3. GC profiles collected for a blank air sample and the gas collected on the Pt electrode. Note that the N_2 and O_2 background signals are always present in our GC system and the injection of H_2 gas sample does not change the N_2/O_2 ratio.

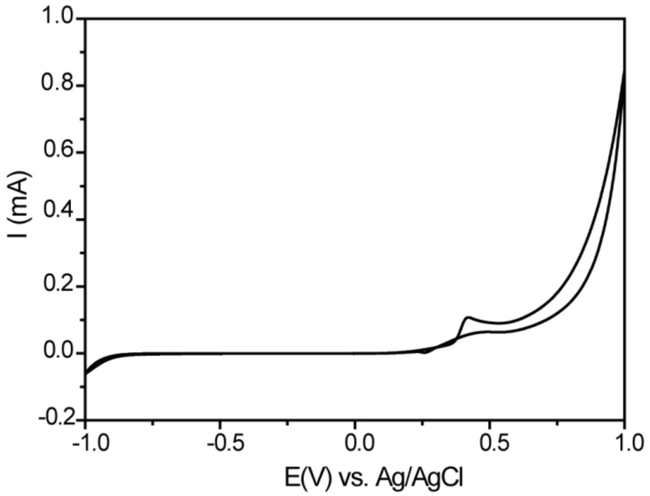

Figure S-4. Cyclic voltammogram collected for Ni-TiO_2 electrode in a urine electrolyte solution, at a scan rate of 50 mV/s .

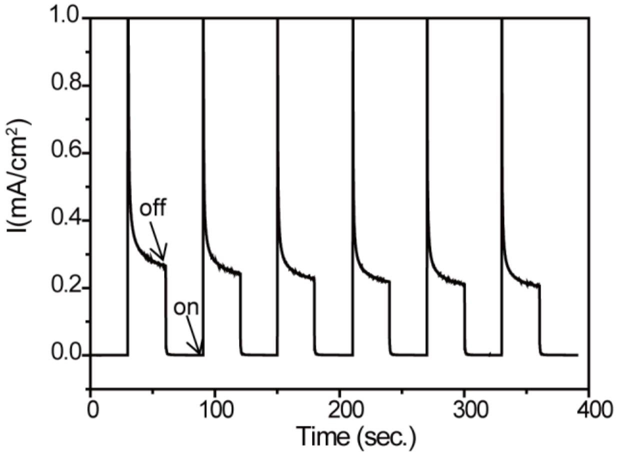

Figure S-5. Photocurrent-time response curve of Ni-TiO_2 in human urine electrolyte solution collected at zero bias in a two-electrode electrochemical cell, under chopped AM 1.5G light illumination (100mW/cm^2).

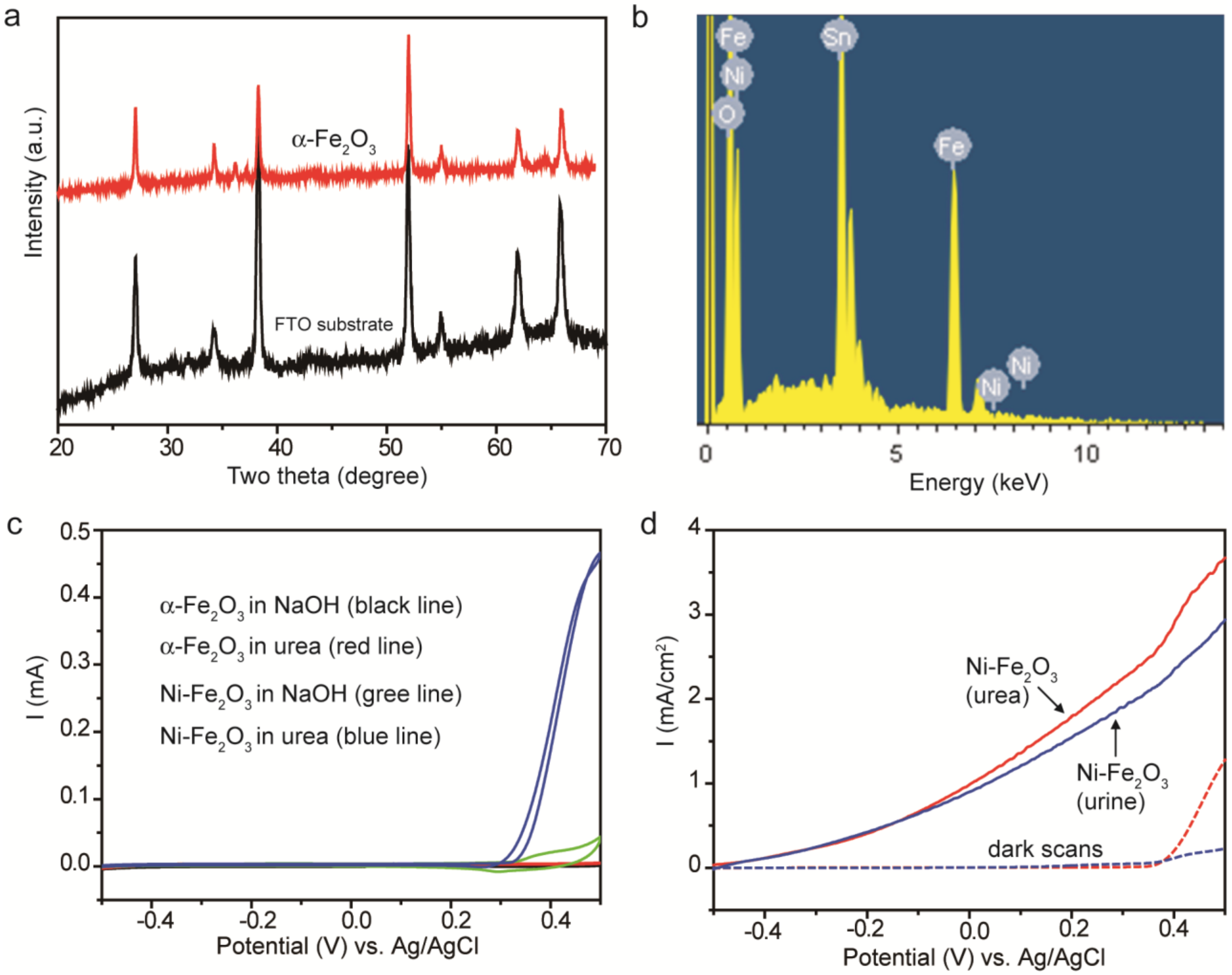

Figure S-6. (a) XRD spectra collected for a blank FTO substrate and hematite nanowires grown on FTO substrate. (b)EDS spectrum of Ni-Fe_2O_3 nanowires. (c) Cyclic voltammograms collected for Ni-Fe_2O_3 electrode in a urine electrolyte solution, at a scan rate of 50 mV/s. (d) Linear sweep voltammograms of Ni-Fe_2O_3 measured in urea and urine electrolyte solutions in the dark (dashed lines) and under AM 1.5G light illumination (100 mW/cm^2), at a scan rate of 50 mV/s.

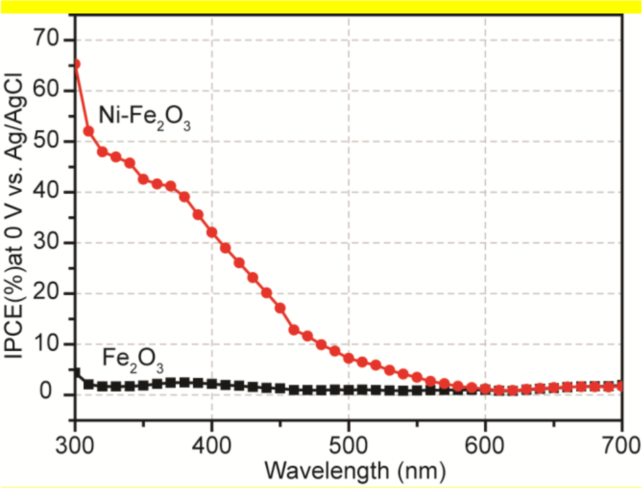

Figure S-7. IPCE spectra collected for Fe_2O_3 and Ni-Fe_2O_3 electrodes at 0 V vs. Ag/AgCl.

References

1. B. Liu and E. S. Aydil, *J. Am. Chem. Soc.*, 2009, **131**, 3985-3990.
2. Y. C. Ling, G. M. Wang, J. Reddy, C. C. Wang, J. Z. Zhang and Y. Li, *Angew. Chem. Int. Ed.*, 2012, **51**, 4074-4079.