Supporting Information

Electrocatalytic Oxygen and Hydrogen Evolutions at Ni_3B/Fe_2O_3 Nanotube Arrays under Visible Light Radiation

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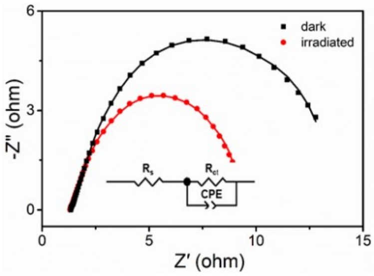

Figure S1. Nyquist plots and simulated curves of Ni_3B/Fe_2O_3 NTAs in dark and under one-sun radiation. The equivalent circuit is shown with the solution resistance denoted as R_s, the charge transfer resistor as R_{ct} and the constant-phase element as CPE.

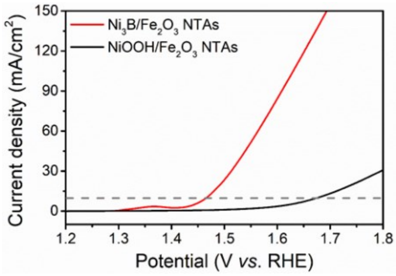

Figure S2. OER polarization curves of Ni_3B/Fe_2O_3 NTAs and $NiOOH/Fe_2O_3$ NTAs under one-sun radiation.

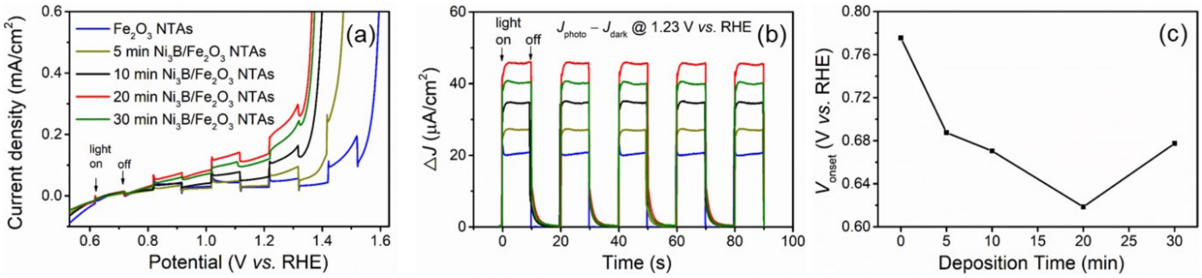

Figure S3. OER (a) polarization curves and (b) chronoamperomograms at 1.23 V at the bare Fe_2O_3 NTAs and Fe_2O_3 NTAs modified with Ni_3B using different deposition times (5, 10, 20, and 30 min) under repeated on-off radiation sequences. (c) The onset potential plotted *vs*. deposition time.

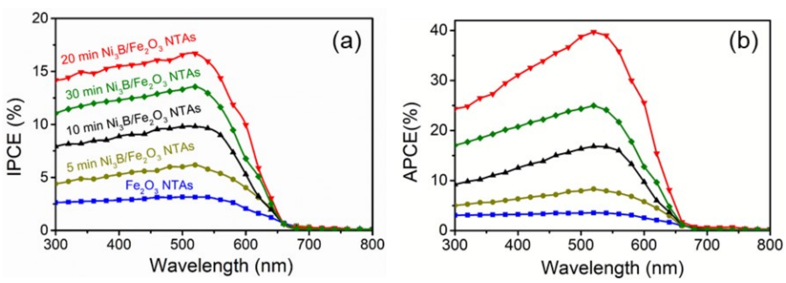

Figure S4. IPCE and APCE spectra at 1.23 V of bare Fe_2O_3 NTAs and Fe_2O_3 NTAs modified with Ni_3B using different deposition times (5, 10, 20, and 30 min).

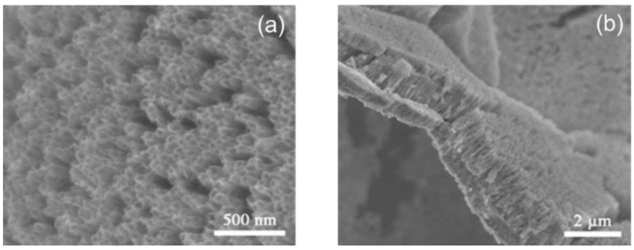

Figure S5. Field emission-SEM images of the top (a) and cross section (b) of Fe_2O_3 NTAs.

In Figure S5, the Fe_2O_3 NTAs have an average inner diameter of 55 nm and a length of 2.05 μm. The vertically oriented and aligned NTAs promote the directional charge transport due to the one-dimensionalilty of the tubes.[1]

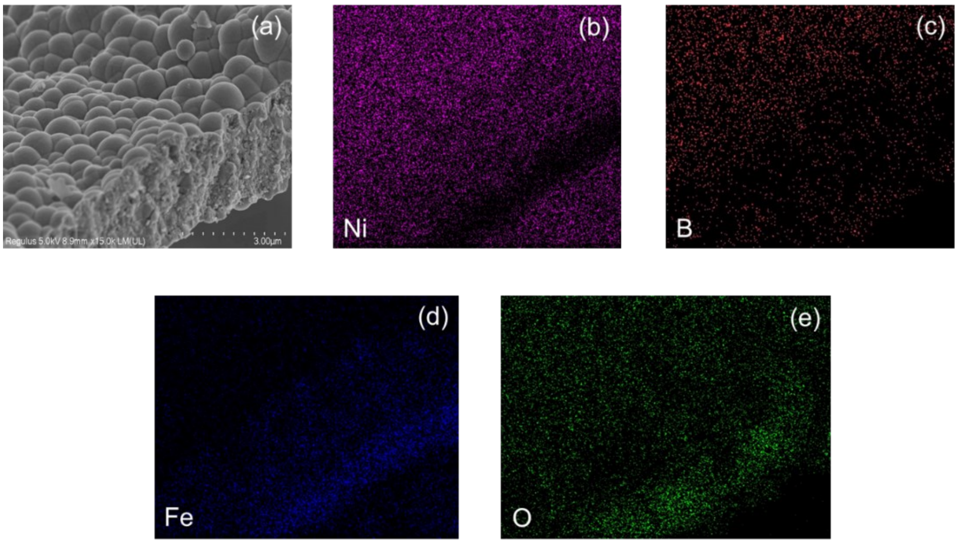

Figure S6. A field emission-SEM image (a) of the Ni_3B/Fe_2O_3 NTAs and the energy dispersive X-ray spectroscopic (EDS) maps corresponding to Ni (b), B (c), Fe (d), and O (e).

Figure S6a is a field emission-SEM image of the cross section of a Ni_3B/Fe_2O_3 NTA, revealing that the nanotudes have an average thickness of 2.25 μm. The thickness of the Ni_3B layer was determined to be around 0.20 μm from the SEM and EDS elemental mapping analysis (Figure S6b-e).

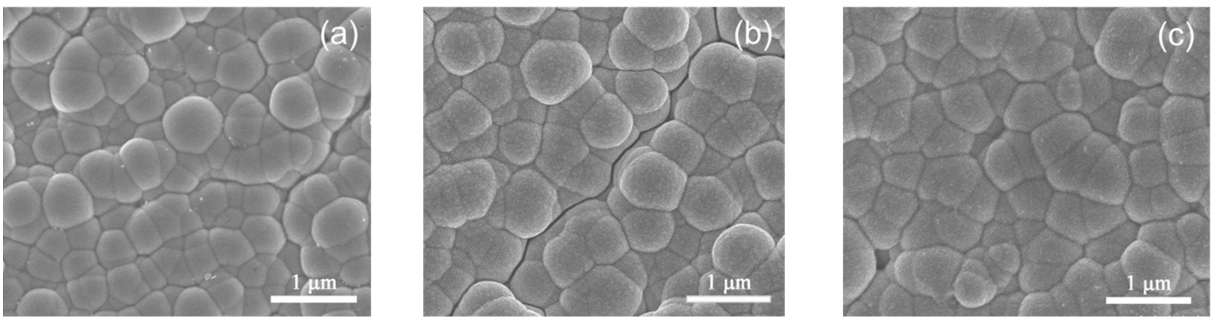

Figure S7. SEM images of Ni_3B/Fe_2O_3 NTAs before (a) and after OER (b) and HER (c).

A field emission-SEM image of a Ni_3B/Fe_2O_3 NTAs (Figure S7a) shows that the entire surface of the Fe foil was uniformly covered with Fe_2O_3 NTAs. After OER, the surface of the Ni_3B/Fe_2O_3 NTAs became rougher and contained numerous nanoparticles (Figure S7b). A closer examination reveals that the nanoparticles are 40 ± 10 nm in diameter. Such a morphological change is likely originated from the Ni_3B oxidation.[2, 3] After HER in alkaline solution, some small burr-like structures covered the Ni_3B/Fe_2O_3 NTAs (Figure S7c).

Table S1. Calculated values of the solution resistor *(R_s)*, charge transfer resistor (R_{ct}) and constant phase element (CPE) on the fitted equivalent circuit of Ni_3B/Fe_2O_3 NTAs in dark and under one-sun radiation.

Condition	R_s (Ω)	R_{ct} (Ω)	CPE (mF/cm^2)
Under irradiation	1.33	8.44	34.93
In dark	1.36	13.17	33.56

Table S2. Best fitted parameters of time-resolved photoluminescence.

Samples	Decay lifetimes (ns)			Fractional contribution			Average lifetimes
	τ_1	τ_2	τ_3	f_1	f_2	f_3	($\tau_{Avg.}$, ns)
Fe_2O_3 NTAs	7.50	55.54	1.33	0.14	0.04	0.82	4.36
Ni_3B/Fe_2O_3 NTAs	7.79	48.05	1.55	0.14	0.04	0.82	4.28

Reference

1. T. J. LaTempa, X. Feng, M. Paulose and C. A. Grimes, *J. Phys. Chem. C*, 2009, **113**, 16293−16298.
2. H. Li, P. Wen, Q. Li, C. Dun, J. Xing, C. Lu, S. Adhikari, L. Jiang, D. L. Carroll and S. M. Geyer, *Adv. Energy Mater.*, 2017, **7**, 1700513.
3. Z. Chen, Q. Kang, G. Cao, N. Xu, H. Dai and P. Wang, *Int. J. Hydrogen Energ.*, 2018, **43**, 6076−6087.