Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

CeO_2 Nanoarrays Decorated Ce-doped ZnO Nanowire Photoanode for Efficient Hydrogen Production with Glycerol as a Sacrificial Agent

Seungkyu Kim,[a,‡] Eunui An,a,‡ Inhyeok Oh,[a] Jun Beom Hwang,[a] Sehun Seo,[a] Yoonsung Jung,[a] Jun-Cheol Park,[a] Hansol Choi,[a] Chang Hyuck Choi,[b] Sanghan Lee,[*a, c]

a. School of Material Science and Engineering, Gwangju Institute of Science and Technology, Gwangju Institute of Science and Technology, 123 Cheomdan-gwagiro, Buk-gu, Gwangju 61005, Republic Korea, E-mail: sanghan@gist.ac.kr

b. Department of Chemistry, Pohang University of Science and Technology (POSTECH), Pohang 37673, Republic of Korea

c. Research Center for Innovative Energy and Carbon Optimized Synthesis for Chemicals(Inn-ECOSysChem), Gwangju Institute of Science and Technology, 123 Cheomdan-gwagiro, Buk-gu, Gwangju 61005, Republic Korea

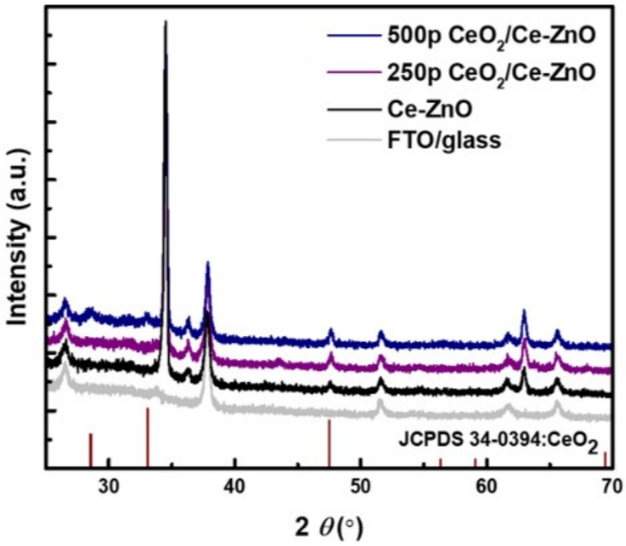

Fig. S1 XRD of FTO substrate, CeO_2 (250 *p*)/FTO, and CeO_2 (250, 500 *p*)/Ce-ZnO electrodes.

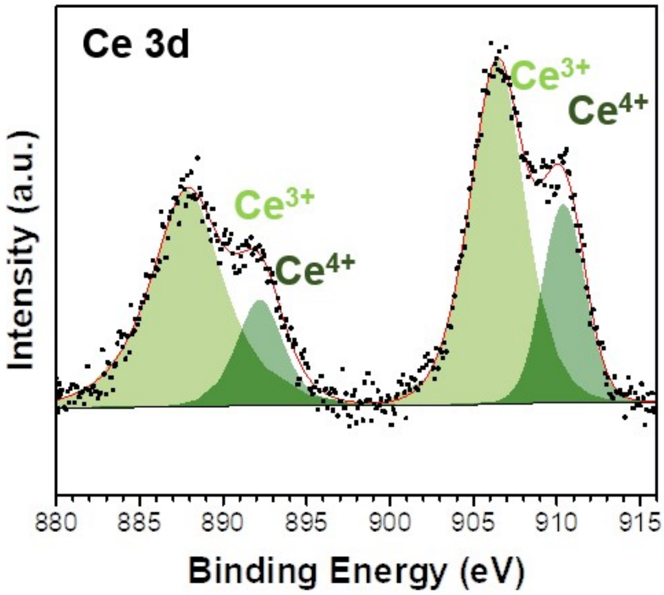

Fig. S2 XPS spectra of Ce-ZnO NWs: HR-XPS spectrum of Ce.

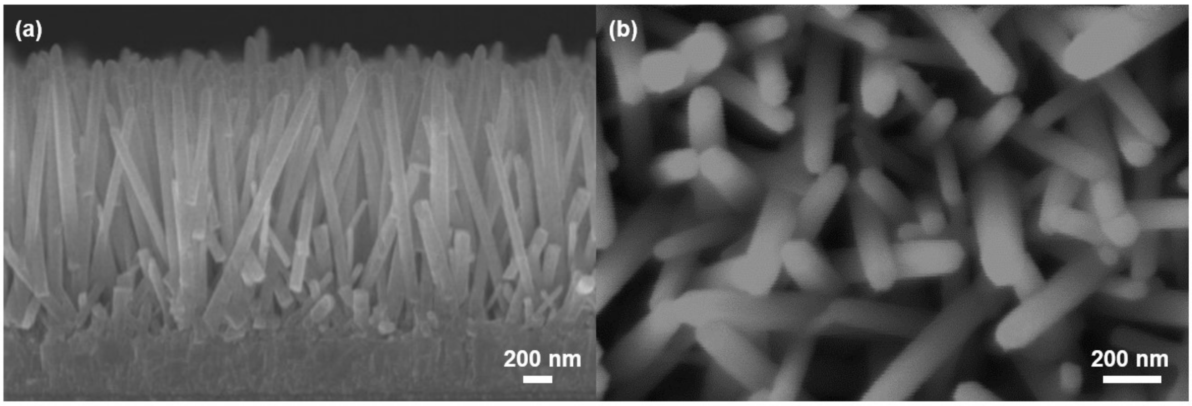

Fig. S3 (a) and (b) SEM images of CeO_2/Ce-ZnO NWs electrode.

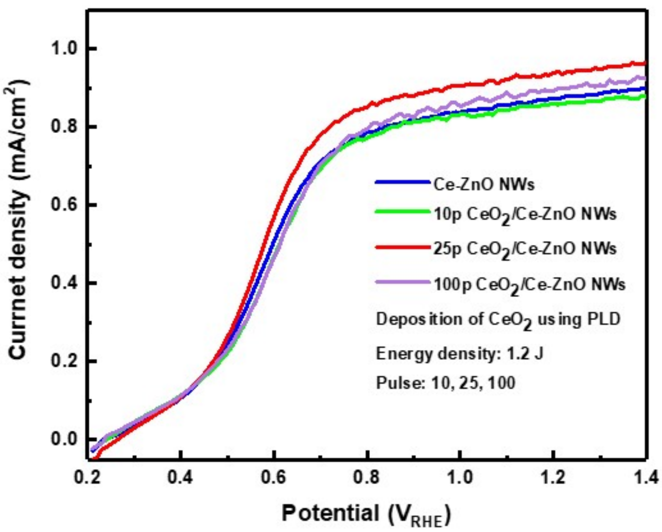

Fig. S4 LSV curves of Ce-ZnO and CeO_2(10, 25, 100 *p*)/Ce-ZnO NWs electrode in 0.1 M KOH with 0.1 M glycerol

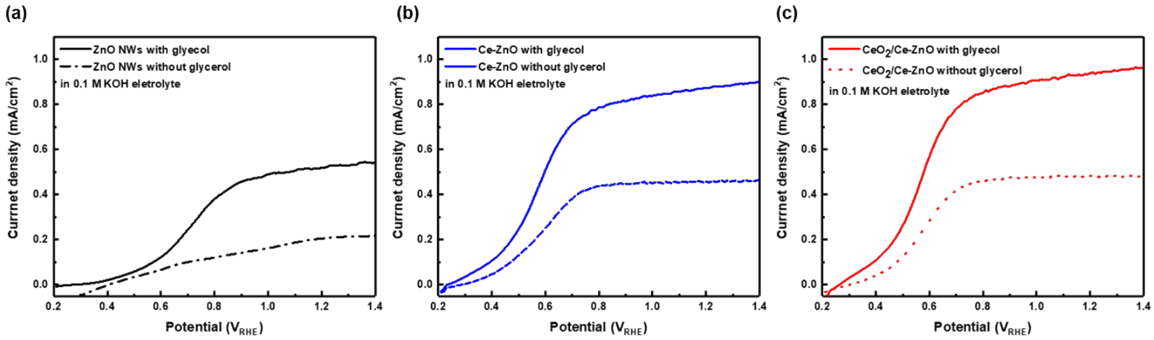

Fig. S5 LSV curves of ZnO NWs, Ce-ZnO, and CeO_2/Ce-ZnO in 0.1 M KOH with(line)/without(dashed) 0.1 M glycerol

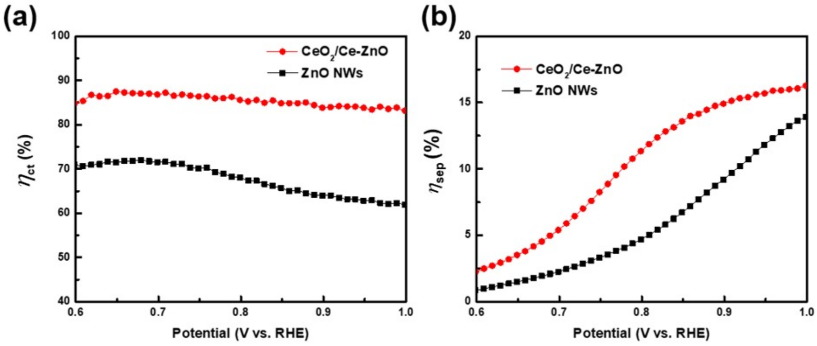

Fig. S6 (a) charge transfer efficiency and (b) charge separation efficiency of bare ZnO NWs and CeO_2 (25 *p*)/Ce-ZnO photoanode.

The above result was calculated using the following equation.

$$\eta_{ct} = J_{H_2O} / J_{glycerol} \quad (1)$$

$$\eta_{sep} = J_{glycerol} / J_{abs} \quad (2)$$

The obtained photocurrent density, J_{H_2O}, could be represented as follows:

$$J_{H_2O} = J_{abs} \times \eta_{sep} \times \eta_{ct} \quad (3)$$

Since there is no hole injection barrier for glycerol oxidation (η_{ct}= 1):

$$J_{glycerol} = J_{abs} \times \eta_{sep} \quad (4)$$

Here, $J_{glycerol}$ is the photocurrent density measured with glycerol photo-oxidation and J_{abs} is the photocurrent density expected when absorbed photons are completely converted into current. Estimated J_{abs} of ZnO NWs and CeO_2/Ce-ZnO are about 2.83 and 5.31 mA/cm^2, respectively

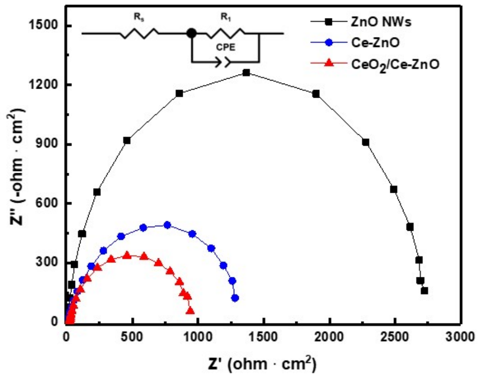

Fig. S7 EIS spectra of bare ZnO NWs, Ce-ZnO, and CeO_2/Ce-ZnO photoanode. Insert shows the equivalent circuit used for it.

Photoanode	R_s ($\Omega\cdot cm^2$)	R_1 ($\Omega\cdot cm^2$)
ZnO NWS	13.0	2711.0
Ce-ZnO	13.8	1299.0
CeO_2/Ce-ZnO	27.7	916.3

Table S1 Comparison of charge transfer resistance results of photoanodes

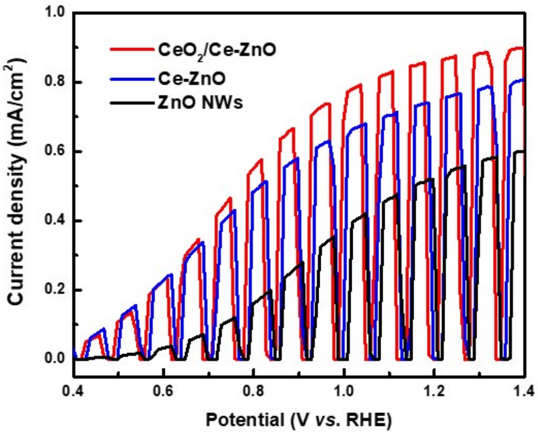

Fig. S8 LSV curves of ZnO NWs, Ce-ZnO, and CeO_2/Ce-ZnO photoanodes under chopped illumination.

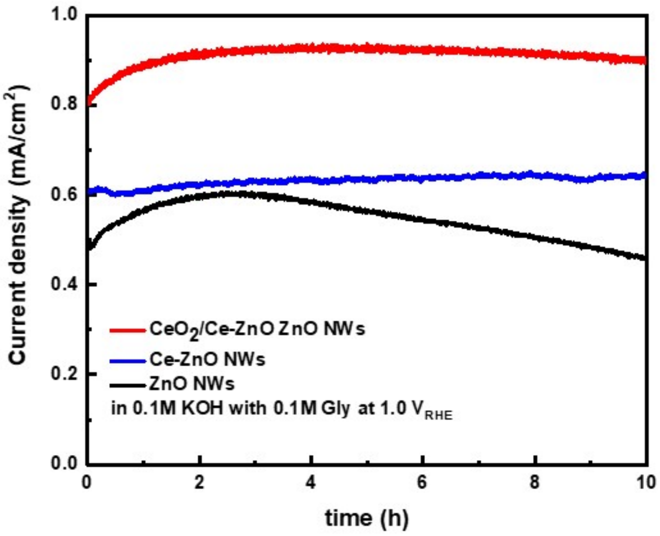

Fig. S9. I-t curves of bare ZnO, Ce-ZnO and CeO_2(25 *p*)/Ce-ZnO photoanode in 0.1 M KOH with 0.1 M glycerol