Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Stabilization of GaAs photoanodes by in-situ deposition of nickel-borate surface catalyst as hole trapping sites

Chaoran Jiang,[a, c] Jiang Wu,[b] Savio J. A. Moniz,[a] Daqian Guo,[b] Mingchu Tang,[b] Qi Jiang,[b] Siming Chen,[b] Huiyun Liu,[b] Aiqin Wang,[c]* Tao Zhang,[c] and Junwang Tang [a]*

a. Department of Chemical Engineering, University College London, Torrington Place, London, WC1E 7JE, UK.

b. Department of Electronic & Electrical Engineering, Torrington Place, London, WC1E 7JE, UK.

c. State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, 116023, China.

∗ Email: (a): junwang.tang@ucl.ac.uk (c): aqwang@dicp.ac.cn

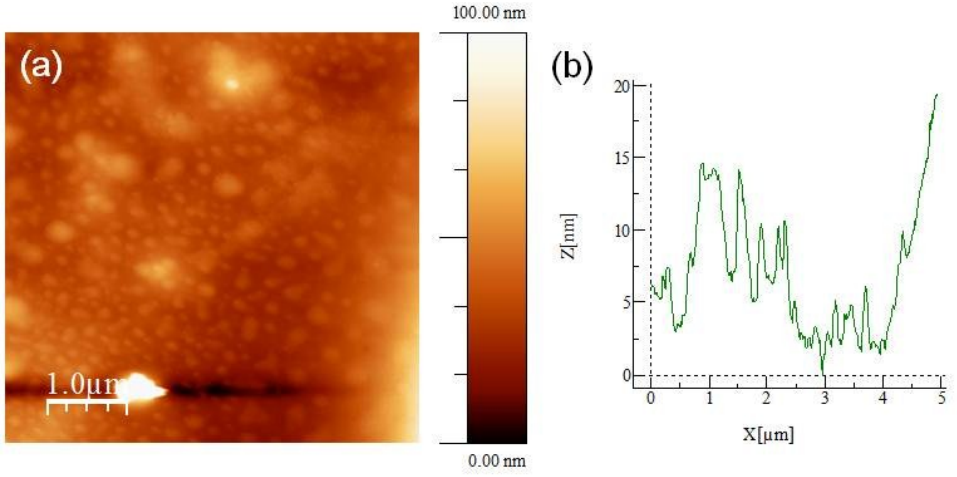

Figure S1: (a) AFM image and (b) Width-height plot of Ni-B/Ga(As)Ox/textured GaAs photoanodes with 0.5h Ni-B photoassisted electro deposition.

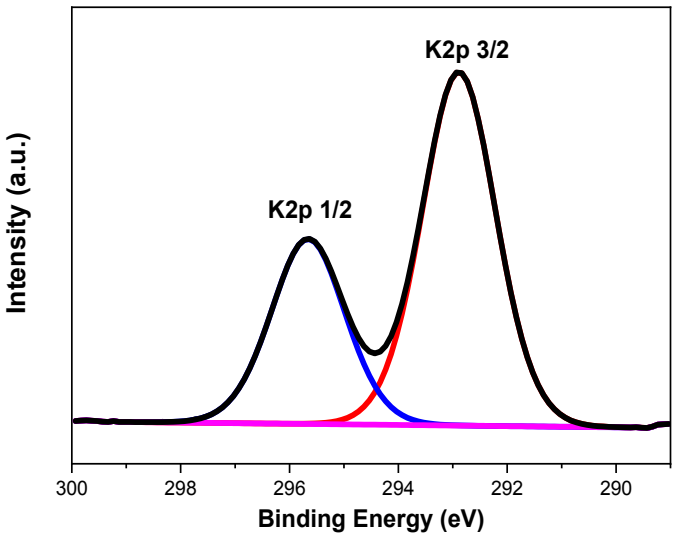

Figure S2: XPS spectra of K 2p of Ni-B/Ga(As)Ox/shallow GaAs photoanode with 0.5 h photoassisted electrodeposited Ni-B catalyst.

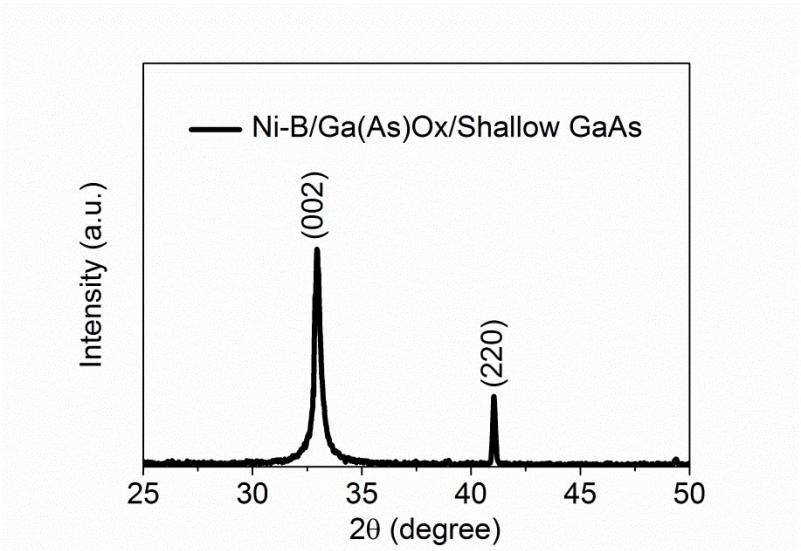

Figure S3: XRD patterns of Ni-B/Ga(As)Ox/shallow GaAs.

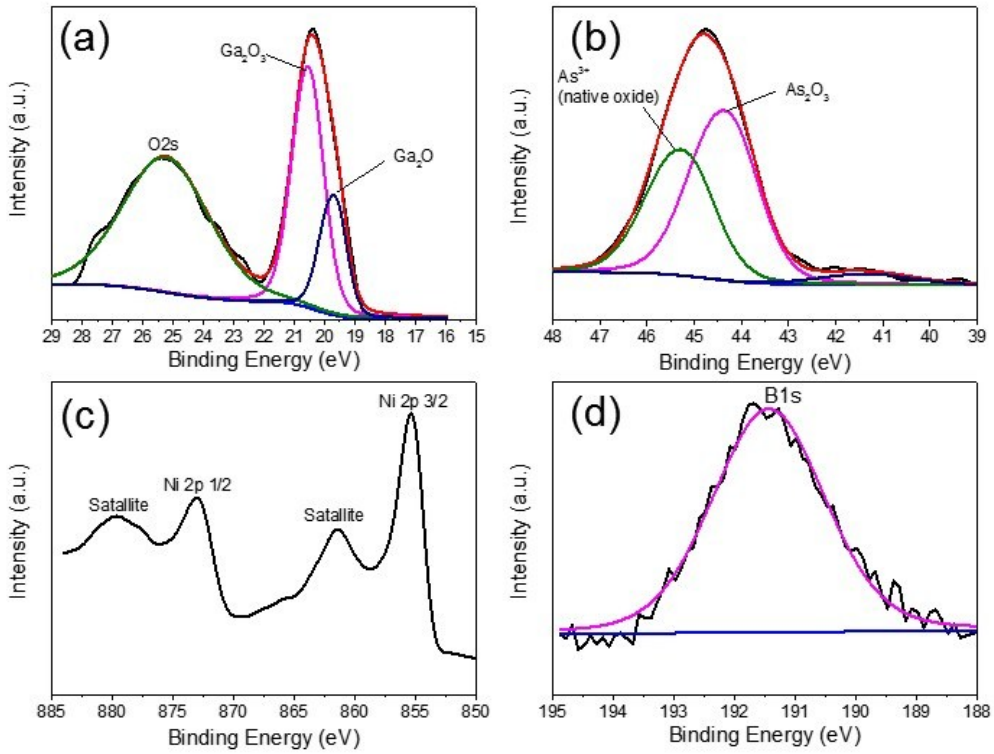

Figure S4*: XPS spectra of Ga 3d, As 3d, Ni 2p, and B 1s for Ni-B/Ga(As)Ox shallow GaAs sample with 1 h photoassisted electrodeposition.*

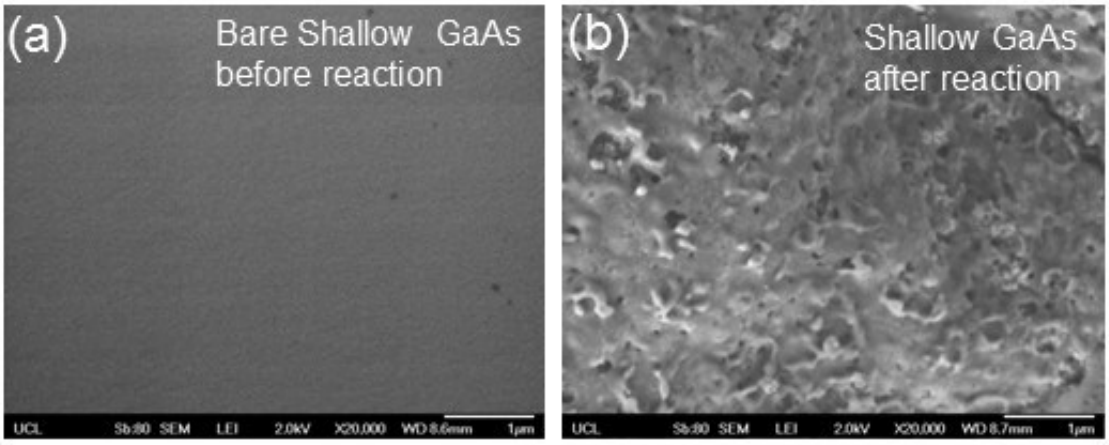

Figure S5: Typical SEM images of bare shallow GaAs photoanodes: (a) before and (b) after 6h photoelectrochemical reaction in 0.1M potassium hydroxide under one sun illumination with a constant applied potential of -0.6 V (vs Ag/AgCl).

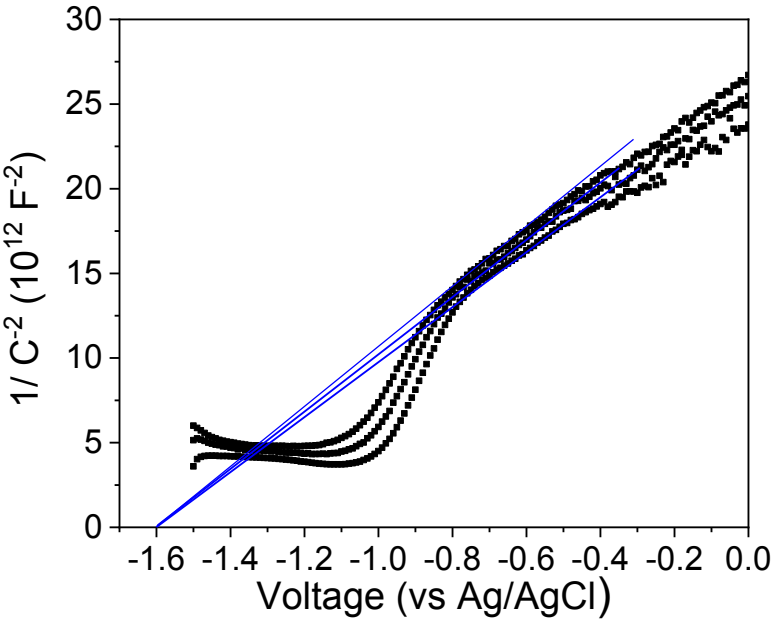

Figure S6: Mott–Schottky plots of Ni-B/GaAsOx/shallow GaAs at 500, 1000 and 2000 Hz in 0.1M KOH solution under dark condition.

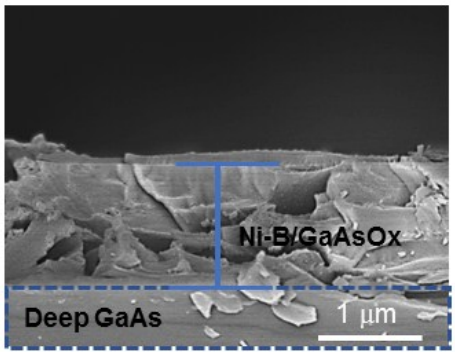

Figure S7: Typical cross-sectional SEM image of Ni-B/Ga(As)Ox/Deep GaAs photoelectrode.

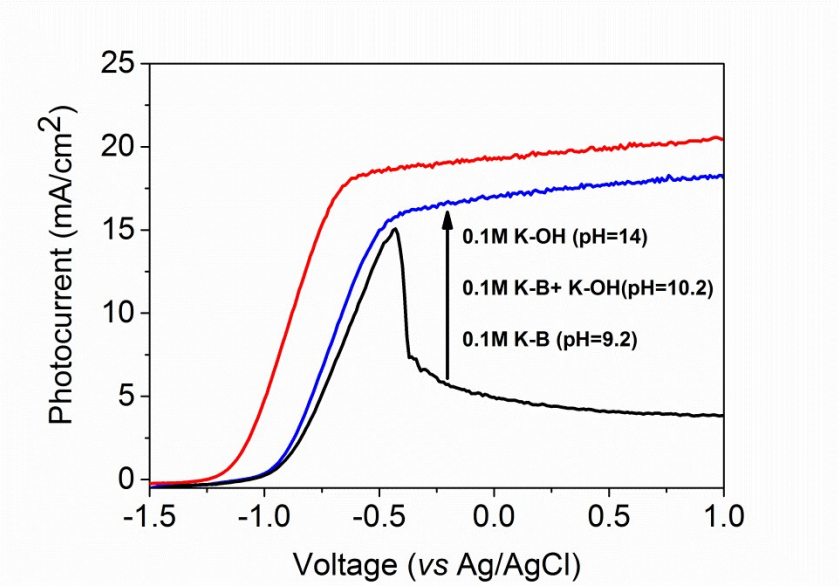

Figure S8: Effect of pH value on current-voltage curve on Ni-B/Ga(As)Ox/ textured GaAs photoanodes with 0.5h Ni-B deposition time.

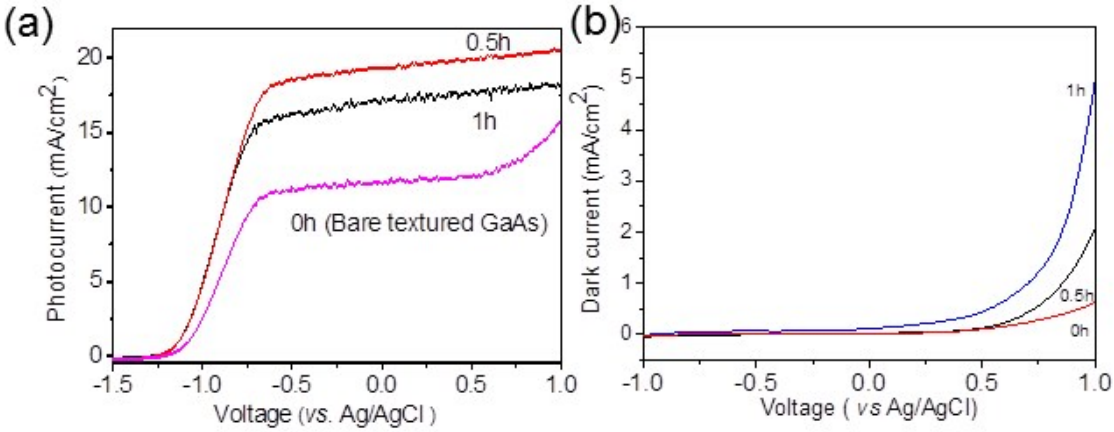

Figure S9: (a) Photocurrent and (b) dark current of Ni-B/Ga(As)Ox/textured GaAs photoanode with varying deposition time; All photoanodes were measured in 0.1M potassium hydroxide (pH=14) under one sun illumination (100 mW/cm^2)

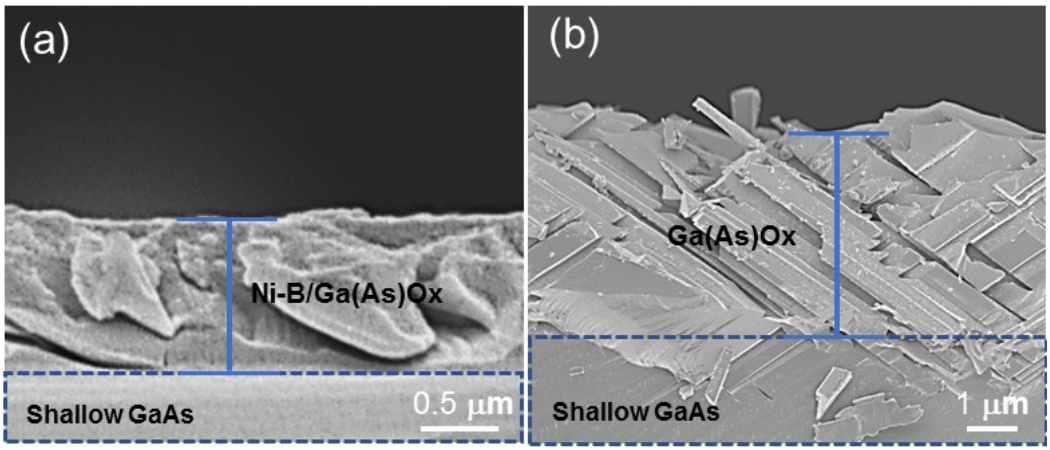

Figure S10: Typical cross-sectional morphology of (a) bare shallow GaAs and (b) Ni-B/Ga(As)Ox/shallow GaAs electrodes after 6h photoelectrochemical water splitting reaction in 0.1 M potassium hydroxide solution under AM 1.5 light irradiation.

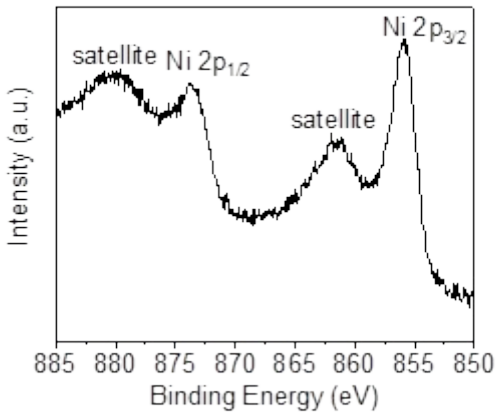

Figure S11: *XPS spectra of Ni 2p for Ni-B/Ga(As)Ox shallow GaAs sample with 0.5 h photoassisted electrodeposition after 6 h PEC reaction in 0.1 M potassium hydroxide（pH=14).*

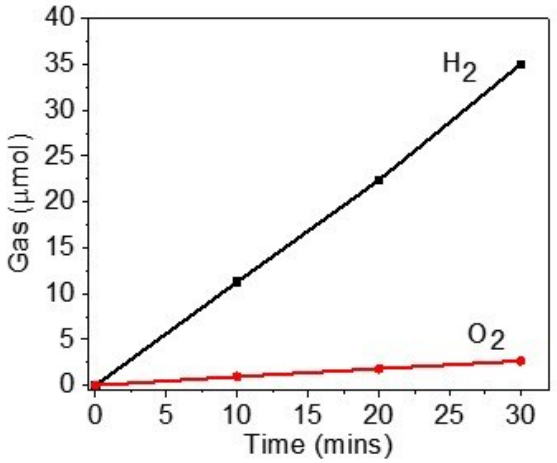

Figure S12: Time profile of gas generation (H_2 and O_2) during photoelectrodechemical water splitting reaction in a gas-tight three electrodes one-compartment cell at constantly applied potential of -0.6 vs Ag/AgCl (Photoanode: Ni-B/Ga(As)Ox/ Shallow GaAs photoanodes; counter electrode: Pt mesh; Reference electrode: Ag/AgCl; electrolyte: 0.1 M potassium hydroxide; light source: AM 1.5 light irradiation ,100 mW/cm^2). The total running charge during 30 mins photocatalytic experiment was 9 C.

The total running charge during the 30 min photoelectroncatalytic experiment is 9 C for the Ni-B/Ga(As)Ox/Shallow GaAs. The total H_2 gas generated is 35 μmol and thus 6.7 C was used for H_2 generation. Therefore, the Faradic efficiency of H_2 generation is 75%, indicating 25% of electrons was used to reduce other species, very likely O_2 in this study which was produced by the photoanode as a single compartment cell was used for the gas measurement. Based on O_2 amount generated (2.67 μmol in 30 mins) and taking account of the oxygen reduced in the one-compartment cell, the Faradic efficiency of O_2 generation is about 36%. In comparison, no oxygen was detected at all for bare shallow GaAs photoanode during the identical measurement (Figure 4c), which

further proves Ni-B surface co-catalyst acts as hole trapping sites on GaAs surface to promote water oxidation reaction and prevent photocorrosion of the photoanode in part although it is not ideal at present. This low Faradic efficiency of O_2 generation indicates that holes generated by the photocatalytic reaction is partially used for other reactions. One possibility is the oxidation of some organic matters originated from the epoxy resin or its surface. [1]

Reference:

[1] K. Ito, S. Ikeda, M.Yoshida, S. Ohta, T.lida, *Bull.Chem.Soc.Jpn*, 1984**, 57**, 583-584