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Supporting Information

Fabrication and enhanced hydrogen evolution reaction performance of a Cu_3BiS_3 nanorods/TiO_2 heterojunction film

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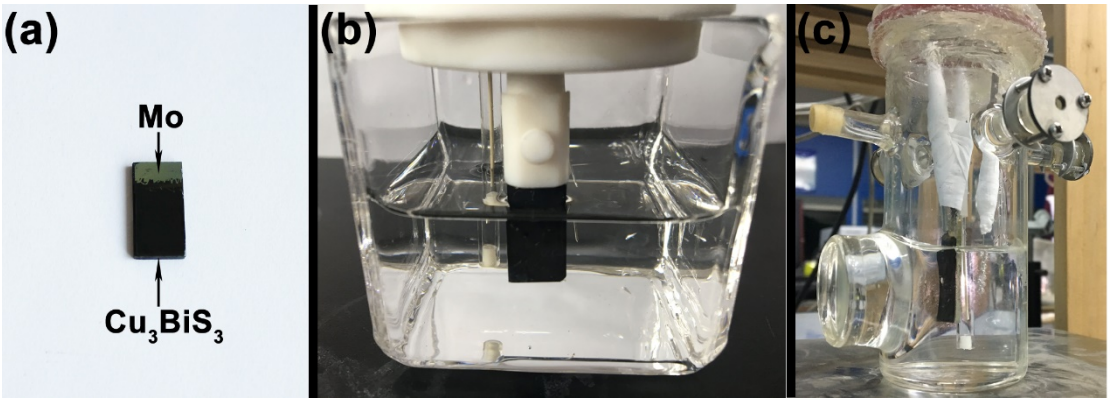

Fig. S1 The digital photos of as-prepared samples (a) after the preparation, (b) in the process of electrochemical test and (c) a self-made photo-reactor.

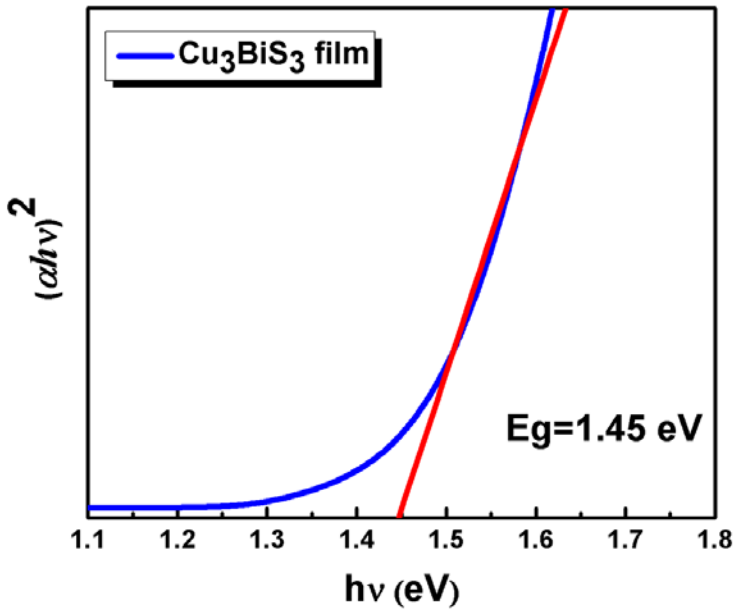

Fig. S2 The plot of $(\alpha h\nu)^2$ versus $h\nu$ for the Cu_3BiS_3 film.

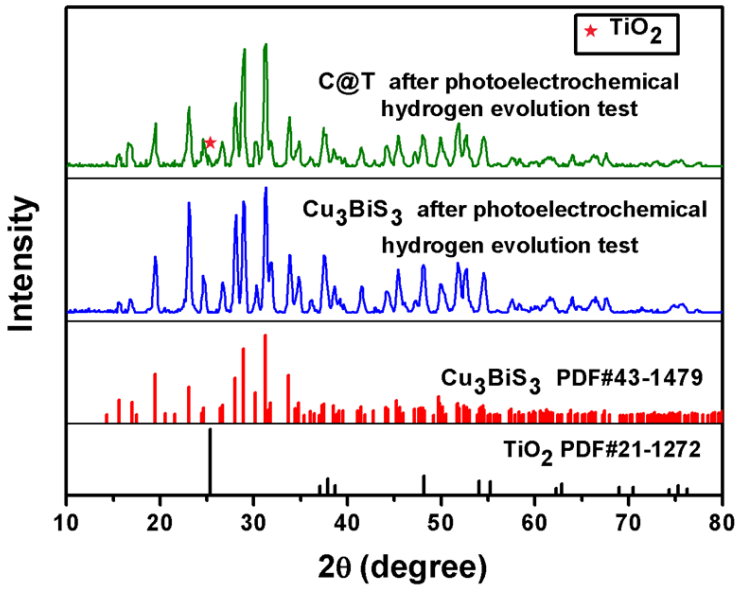

Fig. S3 XRD patterns of Cu_3BiS_3 film and C@T heterojunction film after photoelectrochemical hydrogen evolution tests.

Mott-Schottky analysis

The capacitance–potential measurement are presented as a M-S plot following the equation below[1,2]:

$$\frac{1}{C^2} = \frac{2}{\varepsilon_0 \varepsilon e N_A A^2}\left(V - V_{fb} - \frac{k_B T}{e}\right) \qquad (1)$$

In equation (1) above, C is the space-charge capacitance of the semiconductor, ε_0 is the permittivity in vacuum, ε is the dielectric constant of Cu_3BiS_3, *e* is the electronic charge, V_{fb} is the flat-band potential, V is the applied potential, N_A is the number density of acceptors in Cu_3BiS_3, T is the absolute temperature, A is area of the electrode and k_B is the Boltzmann constant. The flat band potential (V_{fb}) is determined (equation (2) below) after the thermal correction (k_BT/e) of the intercept (V_0) which is estimated from extrapolating the linear part of the curve to $1/C^2$ equals to zero on the potential axis:

$$V_{fb} = V_0 + \frac{k_B}{e} \qquad (2)$$

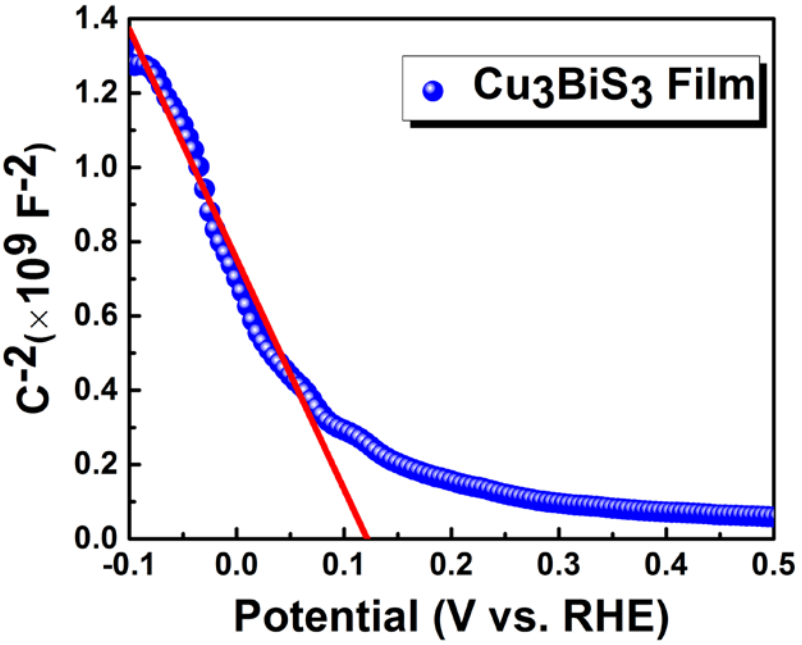

Fig. S4 Mott-Schottky plot of Cu_3BiS_3 nanorods film, and the flat-band potential is obtained from the intercept of the extrapolated line.

References

[1] A. A. Dubale, W. N. Su, A. G. Tamirat, C. J. Pan, B. A. Aragaw, H. M. Chen, C. H. Chen and B. J. Hwang, *J. Mater. Chem. A*, 2014, **2**, 18383.

[2] H. Zhang, Q. Ding, D. He, H. Liu, W. Liu, Z. Li, B. Yang, X. Zhang, L. Lei and S. Jin, *Energy Environ. Sci.*, 2016, **9**, 3113.