Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting information

Gold Nanoparticles Decorated Bismuth Sulfide Nanorods for Enhanced Photoelectrochemical Hydrogen Production

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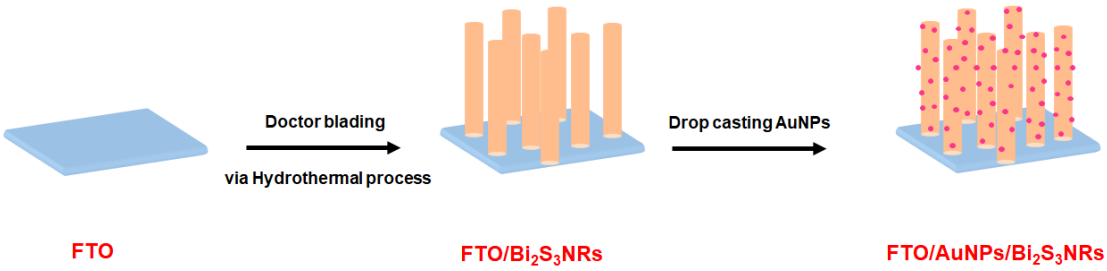
Scheme S1. Procedure for the synthesis of AuNPs/Bi_2S_3NRs composite film.



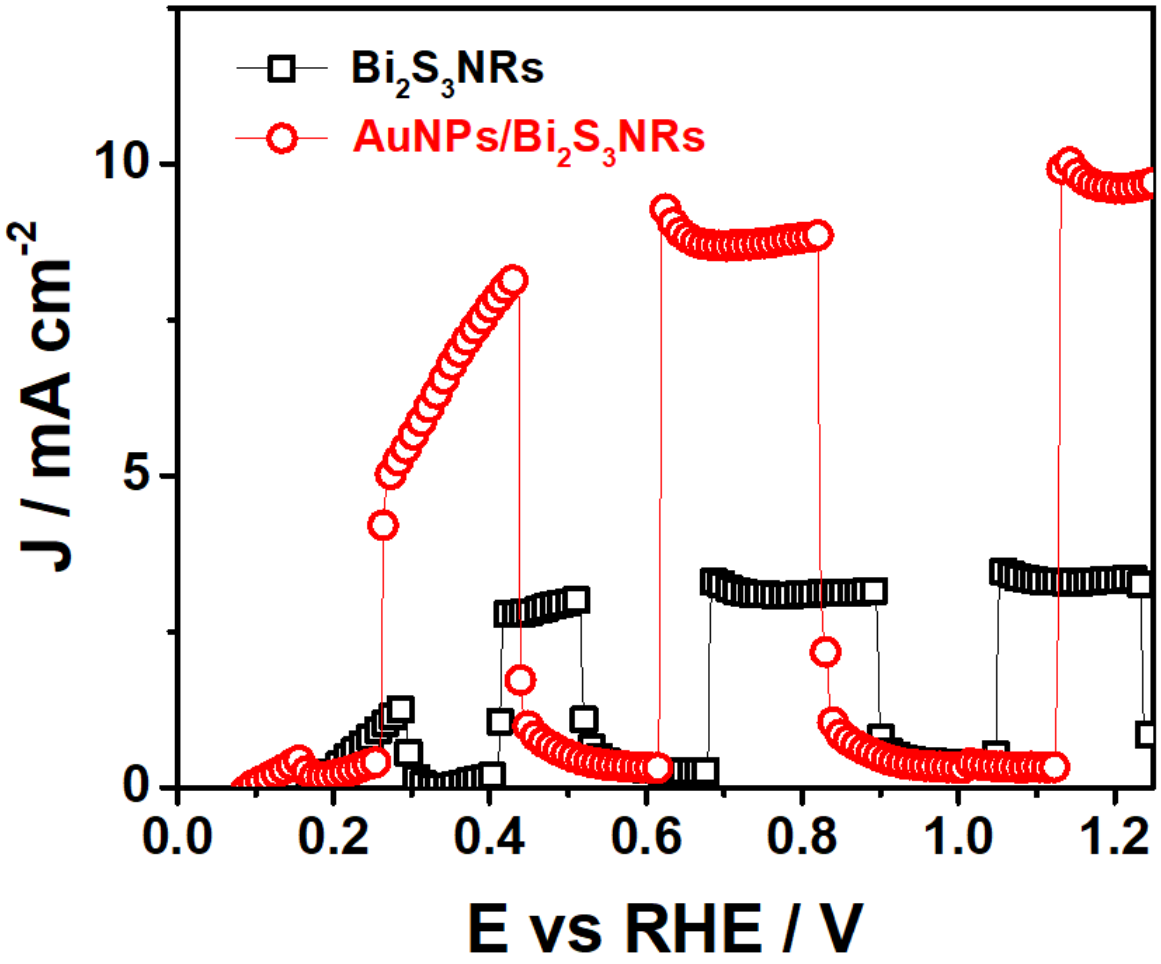


Figure S1. LSV plots of Bi_2S_3NRs and AuNPs/Bi_2S_3NRs as working electrodes, 0.1 M Na_2S and 0.1 M Na_2SO_3 as an electrolyte solution and Pt as a counter electrode under chopped light illumination.

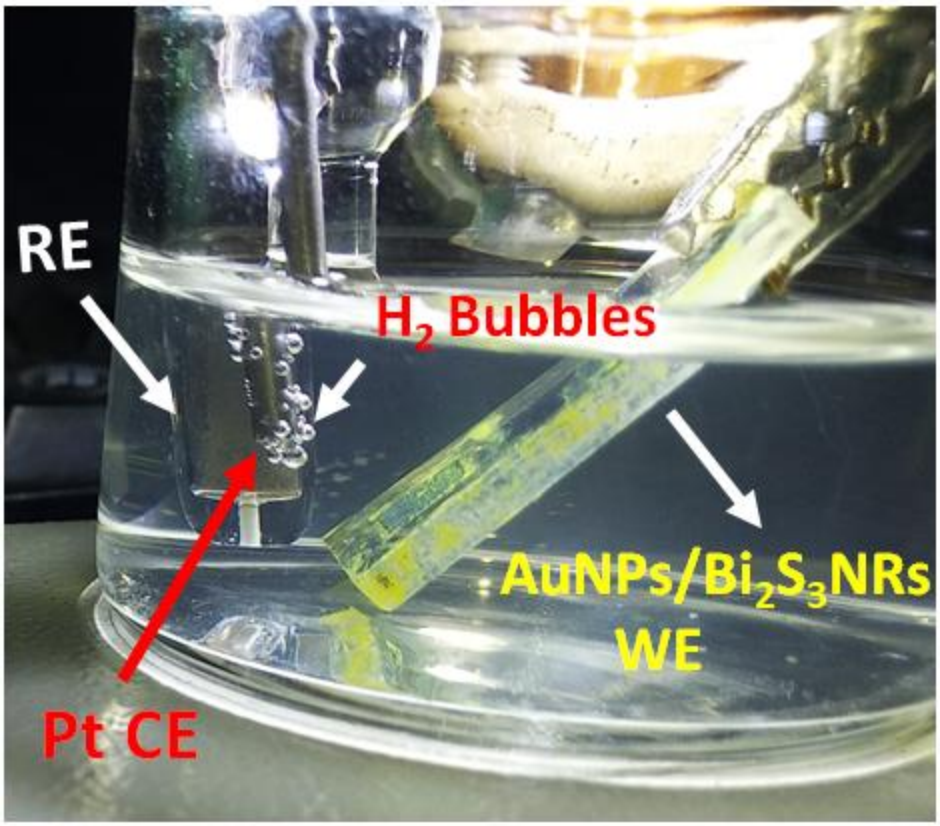


Figure S2. PEC measurements showing the evolution of H_2 bubbles at the Pt counter electrode of AuNPs/Bi_2S_3NRs photoanode under solar light irradiation.

CV plots of CE components for band diagram

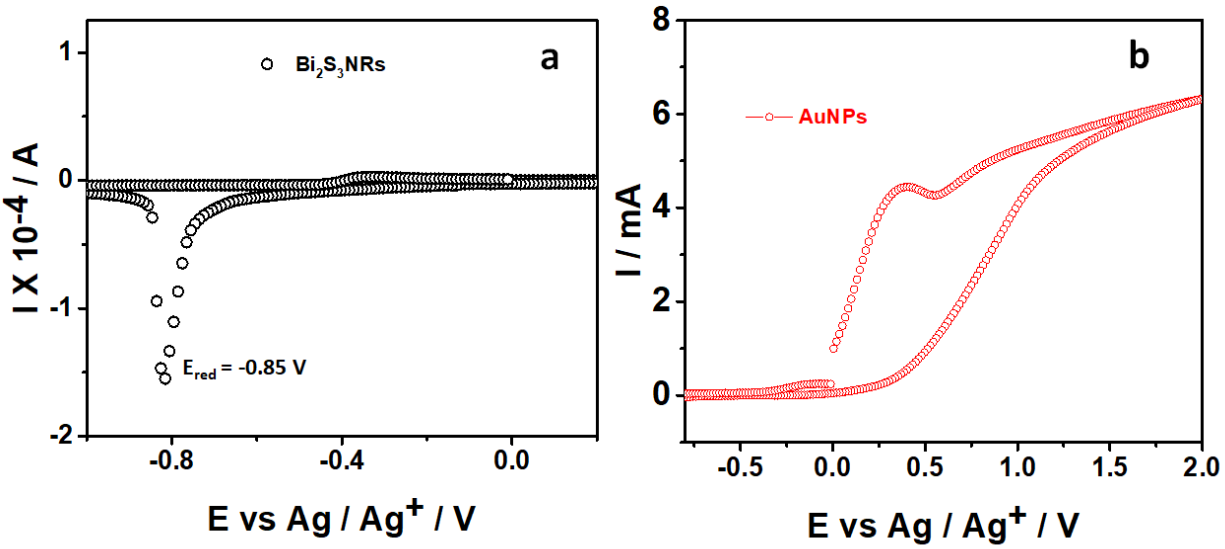


Figure. S3 CV plots of (a) Bi_2S_3NRs and (b) AuNPs in a 0.1 M KOH electrolyte, with Pt as CE, and Ag/AgCl/KCl as the reference.

Calculations of reduction and oxidation peak potentials and Fermi levels:

For Bi_2S_3:
E_{CB} = -1.04 vs Ag/AgCl/KCl
E_{NHE} = -1.04 V + 0.2 V (E^o of Ag/Ag^+) = -0.84 V
We converted V (volts) into eV (electron volts),
Therefore E_{red} = -4.5 eV (0 V vs NHE) – (-0.84 V) = -3.66 eV (CB)
This value is equal to the CB or LUMO position of Bi_2S_3. Then the VB or the HOMO position of Bi_2S_3 was obtained by the addition of the optical bandgap energy value to the CB energy.
E_{red} = -3.66 eV + (-1.58 eV) = -5.24 eV vs NHE (VB)

For AuNPs:
E_{vb} = 0.361 V vs Ag/AgCl/KCl
E_{NHE} = 0.361 V + 0.2 V (E^o of Ag/Ag^+) = 0.558 V
E_F = -4.5 eV -(+ 0.558 V) = –5.058 eV

Photochemical possible reaction mechanism

The possible photoreactions at the AuNPs/Bi_2S_3NRs photoanode and Pt CE respectively are summarized as follows

$$Au/Bi_2S_3 + h\nu \longrightarrow Au^*\text{-}Bi_2S_3^* \quad (1)$$

$$Au^*\text{-}Bi_2S_3^* \longrightarrow Au^+\text{-}Bi_2S_3\,(e^-_{CB}) \quad (2)$$

$$SO_3^{2-} + H_2O + 2h^+_{VB} \longrightarrow SO_4^{2-} + 2H^+ \quad (3)$$

$$2S^{2-} + 2h^+_{VB} \longrightarrow S_2^{2-} \quad (4)$$

$$SO_3^{2-} + S_2^{2-} \longrightarrow S_2O_3^{2-} + S^{2-} \quad (5)$$

$$SO_3^{2-} + S^{2-} + 2h^+_{VB} \longrightarrow S_2O_3^{2-} \quad (6)$$

$$2H^+ + 2e^-_{CB} \longrightarrow H_2 \quad (7)$$