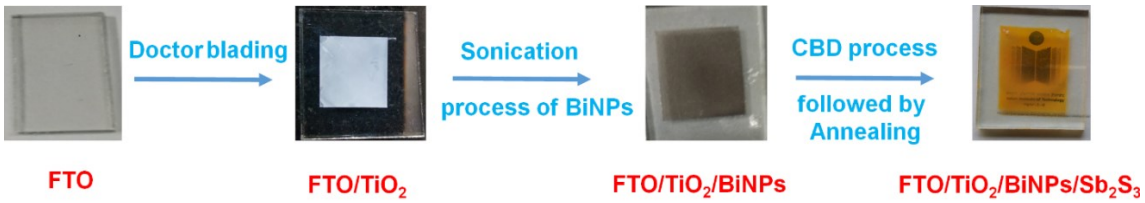
Electronic Supplementary Material (ESI) for Nanoscale Advances.

Supporting Information



Scheme S1. The sequential deposition of TiO_2/BiNP/Sb_2S_3 photoanode.

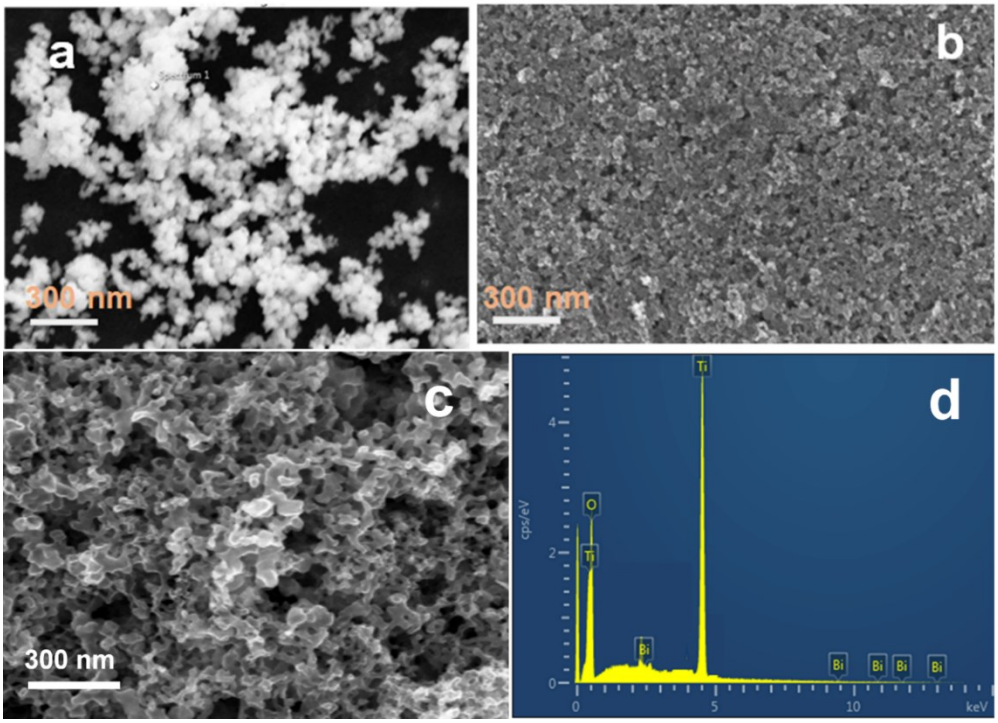


Figure S1. (a-c) FESEM images of BiNPs and TiO_2/Sb_2S_3 and TiO_2/BiNP electrodes. (d) EDAX of TiO_2/BiNP electrode.

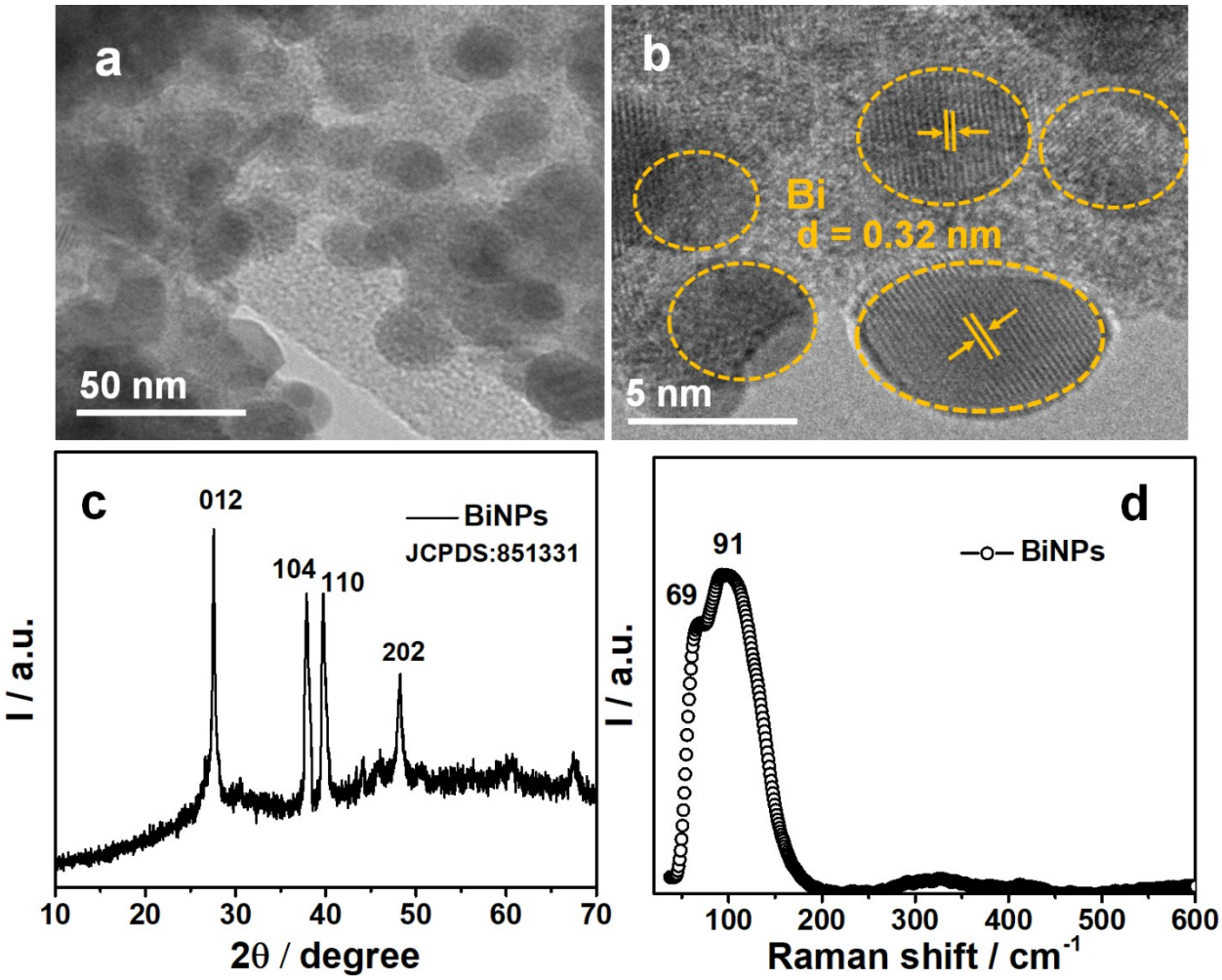


Figure S2. (a) TEM image, (b) HRTEM image, (c) XRD pattern and (d) Raman spectra of BiNPs.

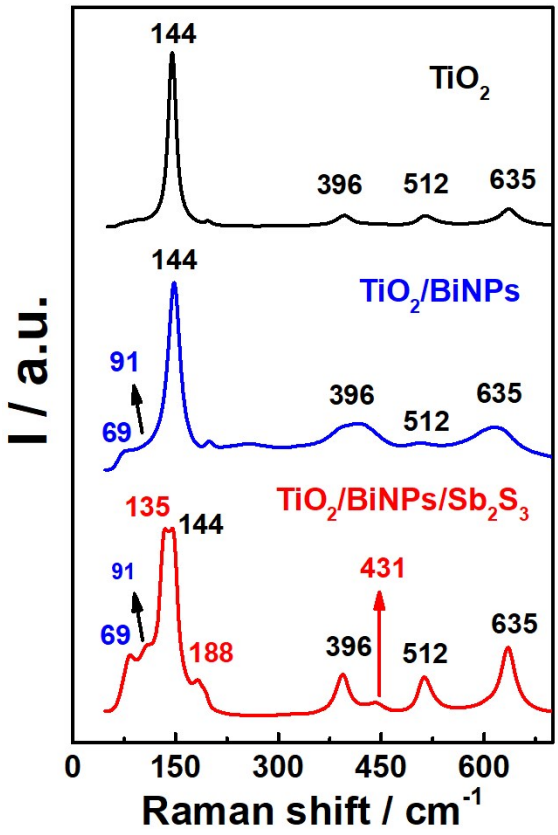


Figure S3. Raman spectra of TiO_2, TiO_2/BiNP and TiO_2/BiNP/Sb_2S_3 samples.

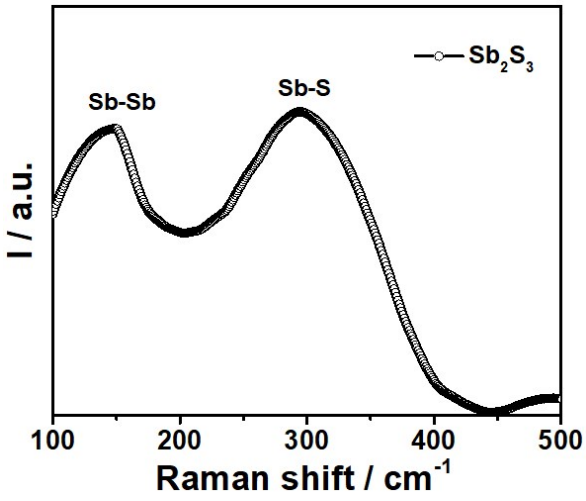


Figure S4. Raman spectra of Sb_2S_3 sample, where 148 cm^{-1} and 294 cm^{-1} bands are associated with Sb-Sb and Sb-S bonding, respectively.

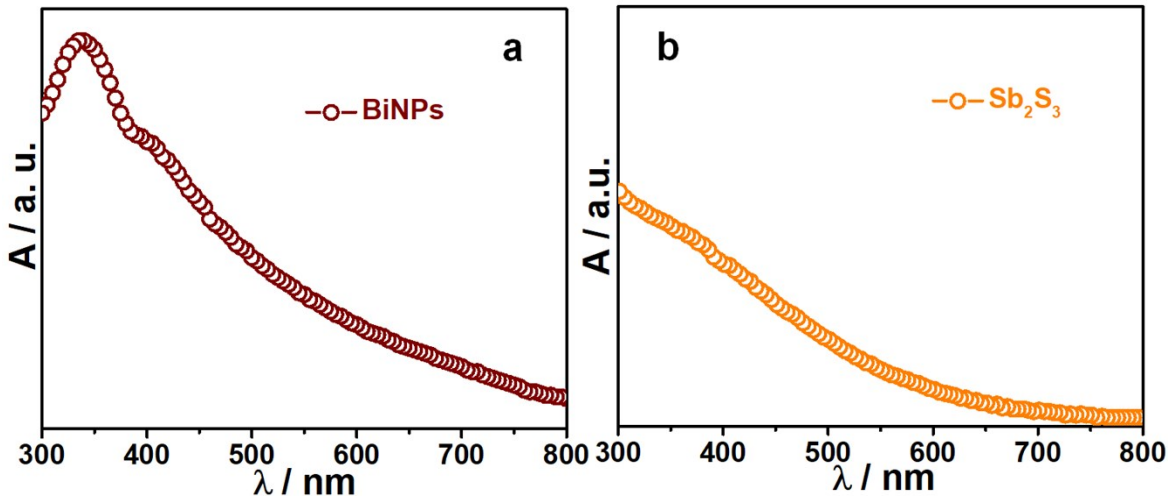


Figure S5. (a) Absorption spectra of BiNP and (b) Sb_2S_3 NP samples.

Solar to hydrogen conversion efficiency:

The solar to hydrogen (STH) conversion efficiencies (η) of the photoelectrodes were calculated using the following equation:

$$\eta = J\,(1.23 - V)/\,P_{light} \qquad (1)$$

where, P_{light}, J and V are the illumination intensity (100 mW cm^{-2}), photocurrent density at the measured bias and applied potential versus RHE, respectively.

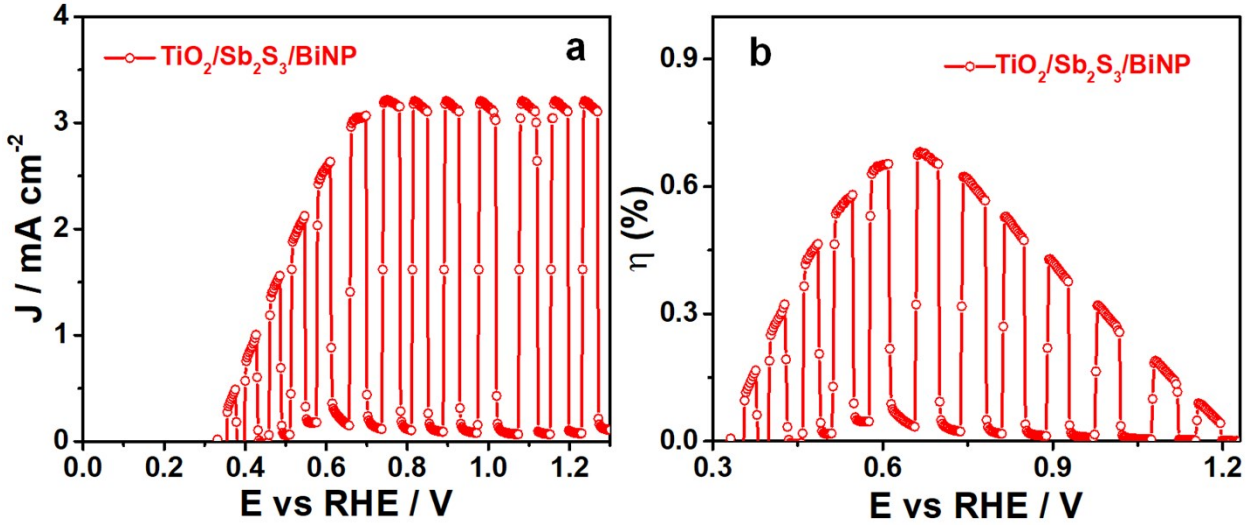


Figure S6. (a) LSV plots and (b) STH efficiency of the TiO_2/Sb_2S_3/BiNP photoelectrode.

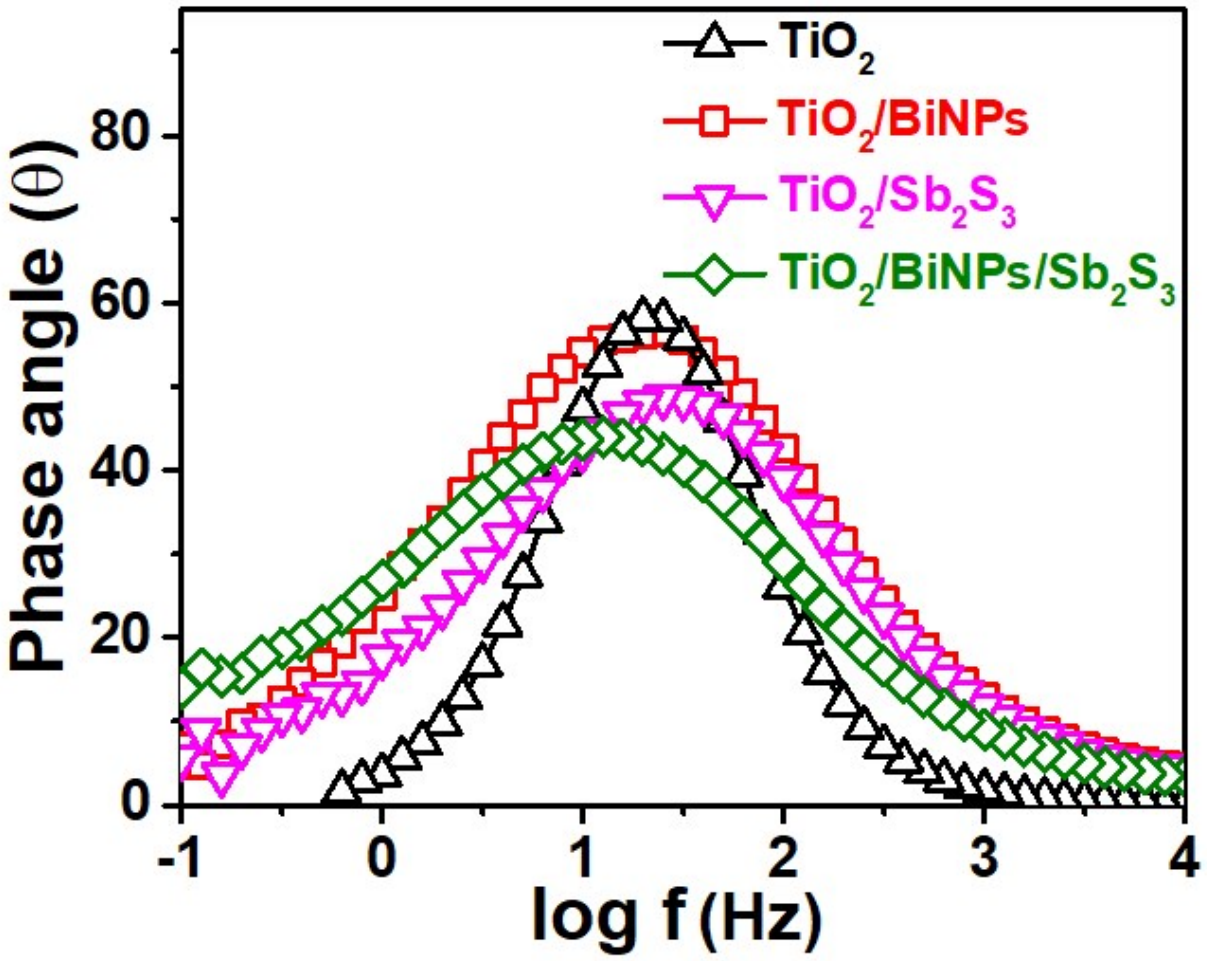


Figure S7. Bode plots of pristine TiO_2, TiO_2/BiNP, TiO_2/Sb_2S_3 and TiO_2/BiNP/Sb_2S_3 electrode.

Table 1. Solar cell parameters of cells with 0.1 M Na_2S electrolyte, with active electrode area of 0.12 to 0.15 cm^2 under 1 sun illumination (100 mW cm^{-2}) with C-fabric as the counter electrode.

Photoanode configuration	V_{oc} **(V)**	J_{sc} **(mA/cm^2)**	**FF(%)**	**η(%)**
(1)TiO_2	**0.42**	**0.15**	**65**	**0.019**
(2) TiO_2/BiNP	**0.54**	**0.56**	**66**	**0.39**
(3)TiO_2/Sb_2S_3	**0.81**	**8.41**	**44**	**2.99**
(4) TiO_2/BiNP/Sb_2S_3	**0.86**	**9.54**	**47**	**3.85**

Table 2. Impedance data after fitting plots of the pristine TiO_2, TiO_2/BiNP, TiO_2/Sb_2S_3 and TiO_2/BiNP/Sb_2S_3 composite photoanodes.

Sample	R_S (Ω)	R_{CT} (Ω)	CPE (μΩ^{-1})
(1) TiO_2	8.1	775	12.4
(2) TiO_2/BiNPs	7.6	215	18.6
(3) TiO_2/Sb_2S_3	5.3	146	24.3
(4) TiO_2/BiNP/Sb_2S_3	3.9	71	26.1

Cyclic voltammograms (CV):

CV of pristine TiO_2, BiNPs and Sb_2S_3 films are shown in Fig. S6 and the position of the CB and VB energy levels were calculated from the oxidation and reduction potential. CV plots of TiO_2, BiNPs and Sb_2S_3 films (as working electrodes), were recorded in an aqueous KOH solution, Pt and Ag/AgCl/KCl as the counter electrode and reference electrode, respectively.

For TiO_2 the conduction band (CB) and the valance band (VB) positions were calculated by using the following method.

E_{red} = -0.96 V versus Ag/AgCl/KCl

Electrode potential of reference electrode = +0.197 V

E_{red} versus NHE (normal hydrogen electrode)

E_{red} = -0.96 V + 0.197 V = -0.763 V (NHE)

We converted V (volts) into eV (electron volts),

Therefore, E_{red} = -4.5 eV (0 V vs NHE) - (-0.76 V) = -3.74 eV (CB)

This value is equal to the CB position of g-C_3N_4. Then the VB position of TiO_2 was obtained by the addition of the optical bandgap energy value to the CB energy.

E_{red} = -3.74 eV + (-3.13 eV) = -6.87 eV (VB)

For Sb_2S_3:

E_{vb} = -1.12 V vs Ag/AgCl/KCl

E_{NHE} = -1.12 V + 0.197 V = -0.923 V

E_F = -4.5 eV - (- 0.92 V) = -3.58eV (CB)

E_{red} = -3.58 eV + (-1.71 eV) = -5.29 eV (VB)

For BiNPs:

E_{vb} = -0.44 V vs Ag/AgCl/KCl

E_{NHE} = -0.44 V + 0.197 V = -0.24 V

E_F = -4.5 eV - (- 0.24 V) = -4.25 eV

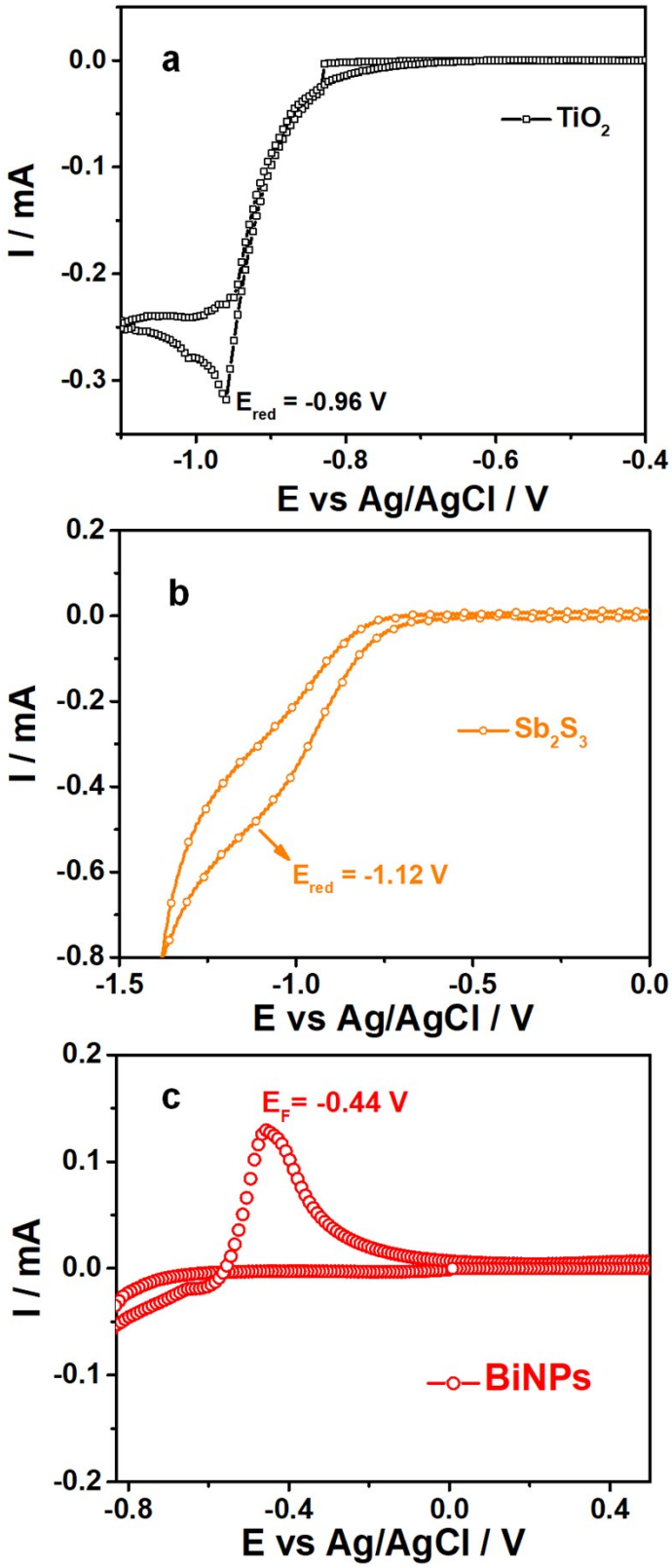


Figure S8. CV of (a) TiO_2, (b) Sb_2S_3 and (c) BiNPs