Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Highly Efficient Electrochemical Reduction of Carbon Dioxide to Formate on Sn Modified Bi_2O_3 Heterostructure

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Experimental Section

The synthesis of $Bi_2O_2CO_3$ precursor and Bi_2O_3 samples: All chemicals are analytical grade and used without further treatment. In a typical procedure, 2g $Bi(NO_3)_2$ $5H_2O$ (Sigma, ACS reagent, ⩾98.0%) is dissolved into 20 ml dilute HNO_3 solution (1 M) under sonication condition. Then, above solution is gradually dropped into 80 ml of Na_2CO_3 (Sigma,⩾99.0%) aqueous solution (0.6 M) under constant stirring. During this process, a large amounts of white precipitate is formed. Next, the above solution is kept at 60 ºC for 6h. Finally, the white products are collected by centrifugation, and washed by water and ethanol for several times before putting into vacuum oven for dry. Then, the Bi_2O_3 sample is prepared by annealing the $Bi_2O_2CO_3$ precursor at furnace under 450 ºC in air for 3min. The final yellow samples are taken out and kept for further characterizations.

The synthesis of Sn modified Bi_2O_3 and SnO_2 samples: Typically, 30 mg Bi_2O_3 sample is firstly dispersed in 10 ml acetone solution by sonication treatment. Then, the above solution is heated to 55 ºC under constant stirring. Next, different amount of stannous chloride (Aldrich, ⩾99.99%) and 0.1g tartaric acid (Alfa Aesar, 99%) are added into above solution. Tin disproportionates in the presence of a tartaric acid. The reaction is kept for 20 min under stirring, the final product can be obtained after it's collected by centrifugation and washed by acetone for several times. The usage of stannous chloride are 0.05, 0.1 and 0.15 mmol to prepare the Sn_L-Bi_2O_3, Sn_M-Bi_2O_3 and Sn_H-Bi_2O_3 products, respectively. The simple SnO_2 nanoparticle is prepared by hydrothermal reaction. Typically, 400 mg $SnCl_4$ $5H_2O$ are put into a mixed solution of 2-propanol (60 ml) and water (20 ml). Then, the solution is adjusted to pH 12 by adding NaOH solution and transfered to autoclave. The reaction is kept for 12 h at 130 ºC. The final powders are collected and washed by water and ethanol solutions.

Structural Characterization

X-ray powder diffraction (XRD) was presented using a Philips X'Pert Pro Super diffractometer with Cu-Kα radiation (λ = 1.54178 Å). The transmission electron microscopy (TEM) was conducted on a HT-7700 field-emission electron microscope operated at an acceleration voltage of 120 kV. The high-resolution TEM (HRTEM) and corresponding energy-dispersive spectroscopy (EDS) mapping analyses were executed on a JEOL JEM-ARF200F TEM/STEM. X-ray photoelectron spectroscopy (XPS) measurements were performed on a PHI5000 Versa Probe II

XPS system by Physical Electronics (PHI) with a detection limit of 1 atomic percent. Monochromatic X-rays were generated by an Al Kα source (1,4867 eV). The diameter of the analyzed area is 10 μm.

Electrochemical Measurements

The electrochemical tests are performed in a gas-tight H-cell with membrane (Nafion 117) on an electrochemical workstation (CHI660B). The Ag/AgCl electrode (saturated KCl), Pt foil and catalysts coated carbon paper are used as reference electrode, counter electrode and working electrode, respectively. Typically, 4 mg of as-prepared sample is dispersed in a mixed solution of 40 μL Nafion and 960 μL ethanol. The solution is kept sonication for 30 min and the catalyst ink is further drop-casted onto a carbon paper. The mass loading of catalyst is about 1 mg cm^{-2}. The test electrolyte is 0.5 M $KHCO_3$ solution. Prior to the measurements, the electrolytes in two compartments are purged with high-pure CO_2 gas for 1 h to reach saturation. All the potentials are converted to reversible hydrogen electrode (RHE) by the equation: $E_{RHE} = E_{Ag/AgCl} + 0.197 + 0.0591 \times pH$. Liquid products are analyzed by ^1H NMR on Bruker DRX 400 Avance MHz spectrometers and the Faradaic efficiency (FE) of liquid sample are calculated by methods: $FEs = 2F \times n/Q = 2F \times n/(I \times t)$. Where n is the total amount of liquid produced (mol) and F is the Faraday constant. The Q is the total amount of charge (C), I is the total current (A) and the t is the applied time.

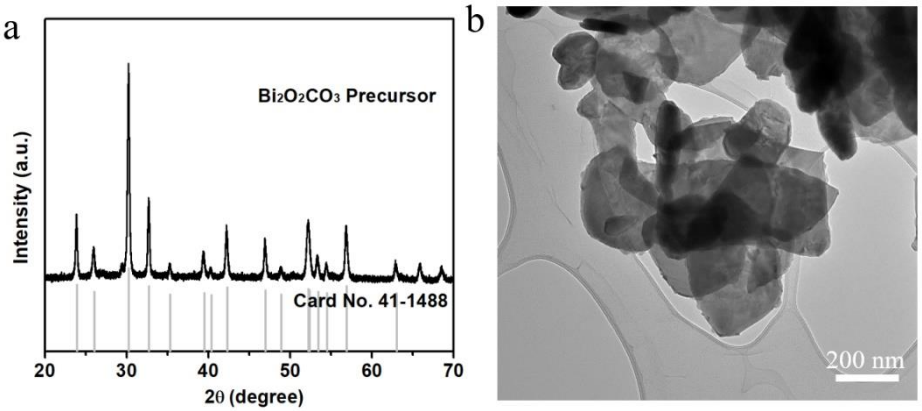

Figure S1 The a) XRD pattern and b) TEM image of $Bi_2O_2CO_3$ precursor.

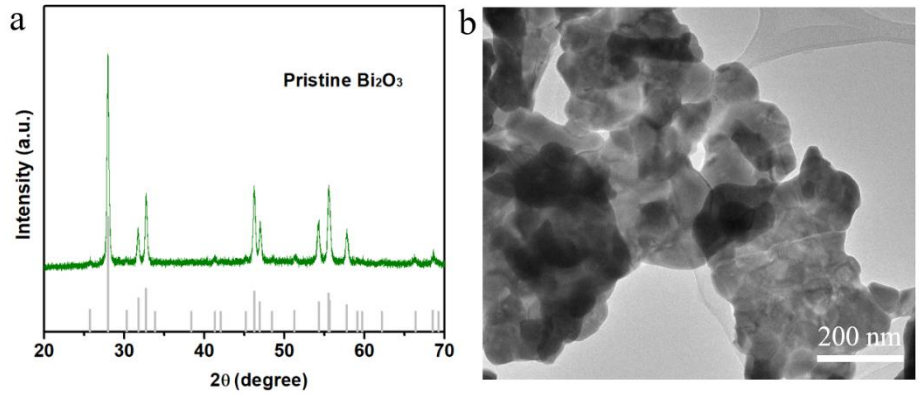

Figure S2 The a) XRD pattern and b) TEM image of pristine Bi_2O_3 sample.

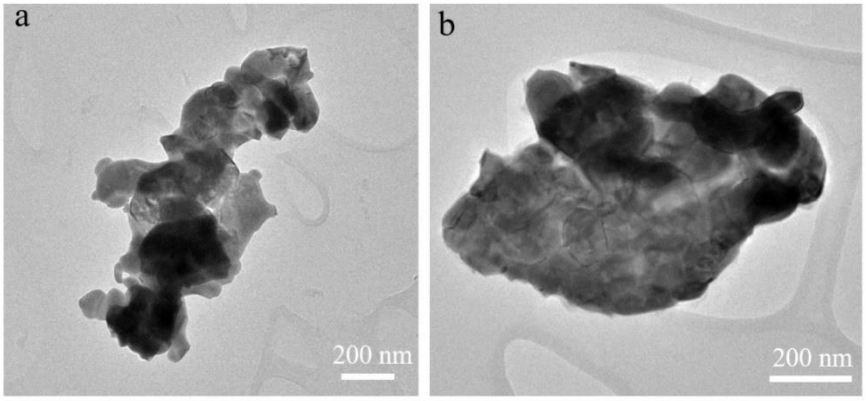

Figure S3 The TEM images of Sn_L-Bi_2O_3 and Sn_H-Bi_2O_3 samples.

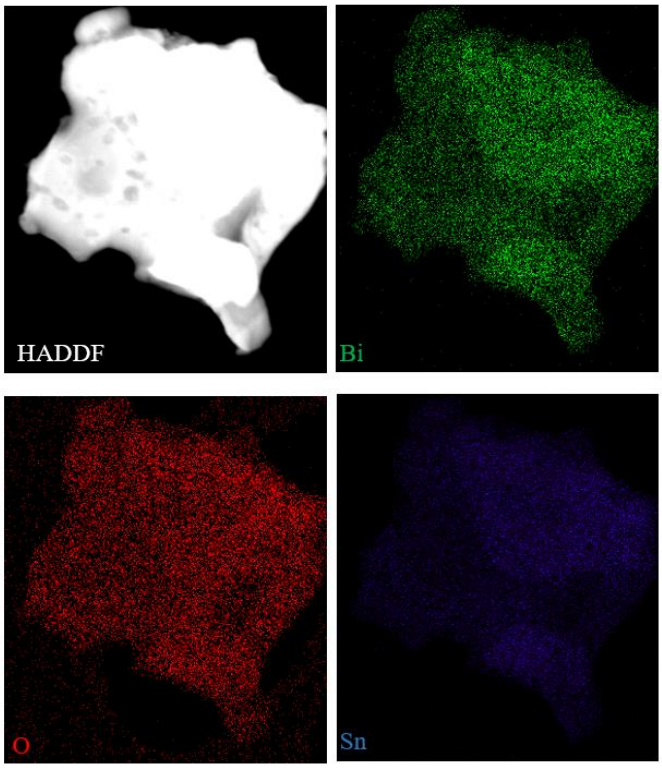

Figure S4 The elemental mapping images of Sn_L-Bi_2O_3 product.

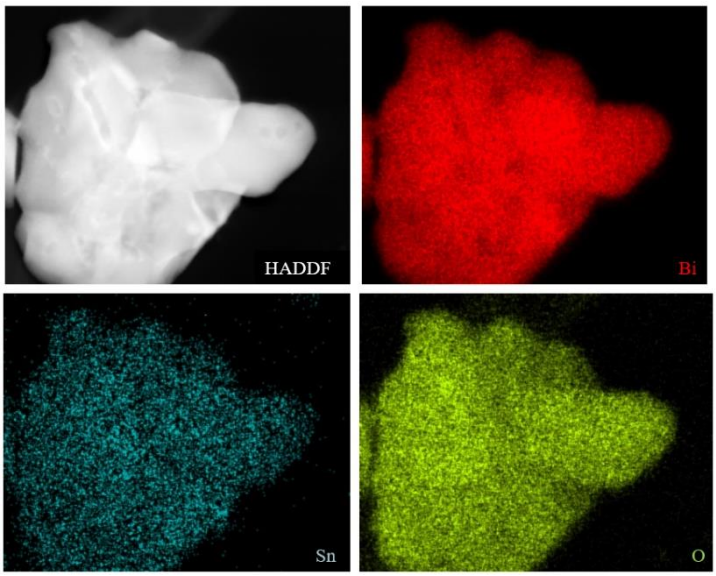

Figure S5 The elemental mapping images of Sn_H-Bi_2O_3 product.

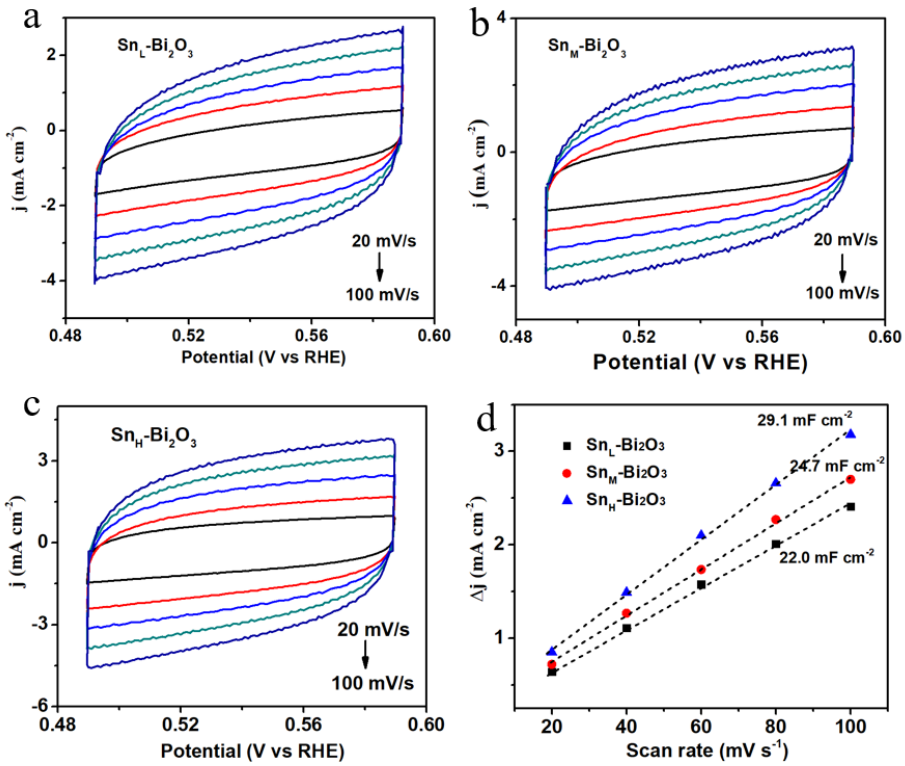

Figure S6 The CV curves vs scan rates for a) Sn_L-Bi_2O_3, b) Sn_M-$Bi_2O_3$and c) Sn_H-Bi_2O_3 catalysts. d) The C_{dl} values for Sn_L-Bi_2O_3, Sn_M-$Bi_2O_3$and Sn_H-Bi_2O_3 catalysts.

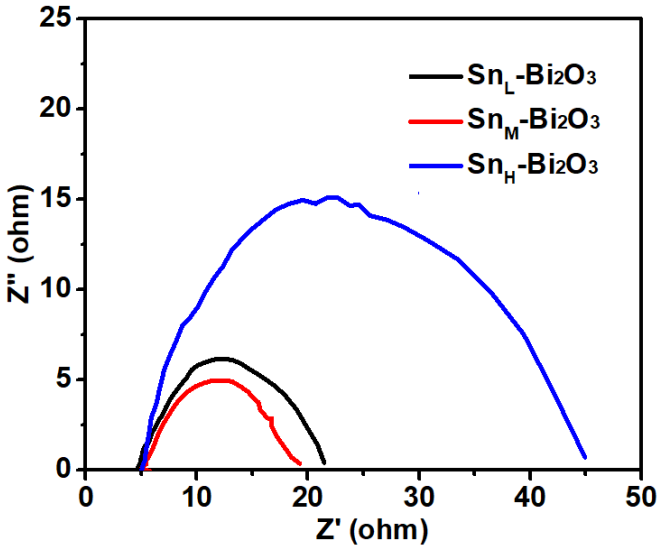

Figure S7 The EIS spectra of Sn_L-Bi_2O_3, Sn_M-Bi_2O_3 and Sn_H-Bi_2O_3.

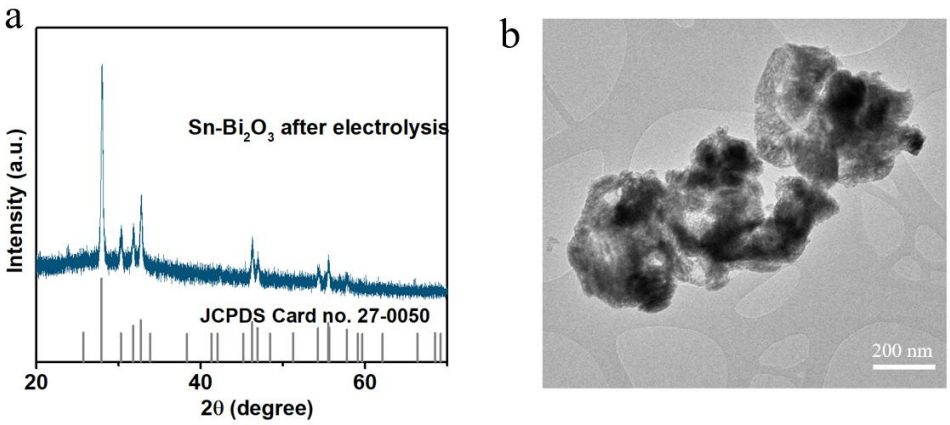

Figure S8 The a) XRD pattern and b) TEM image of Sn_M-Bi_2O_3 sample after CO_2 electrolysis.

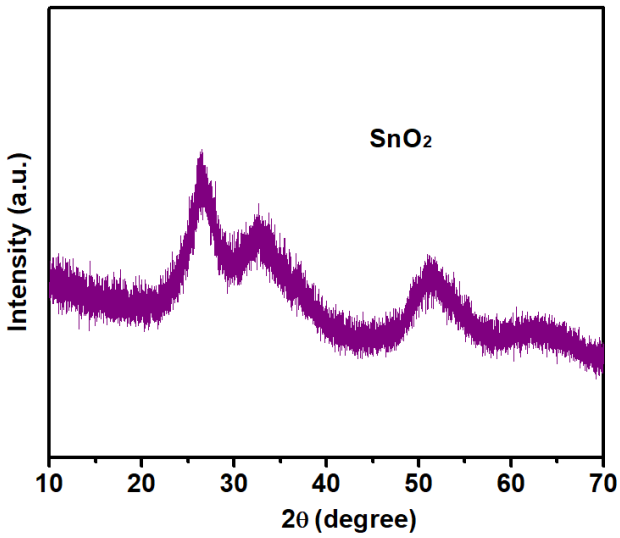

Figure S9 The XRD pattern of SnO_2 sample.

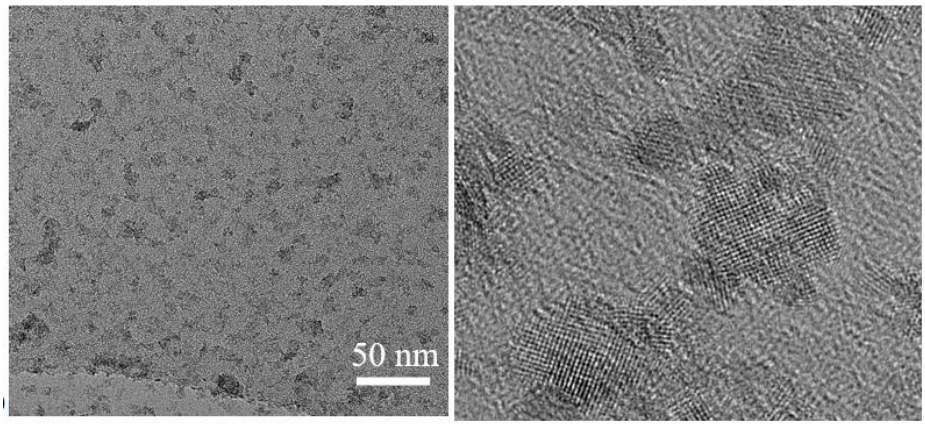

Figure S10 The TEM and HRTEM images of SnO_2 sample.

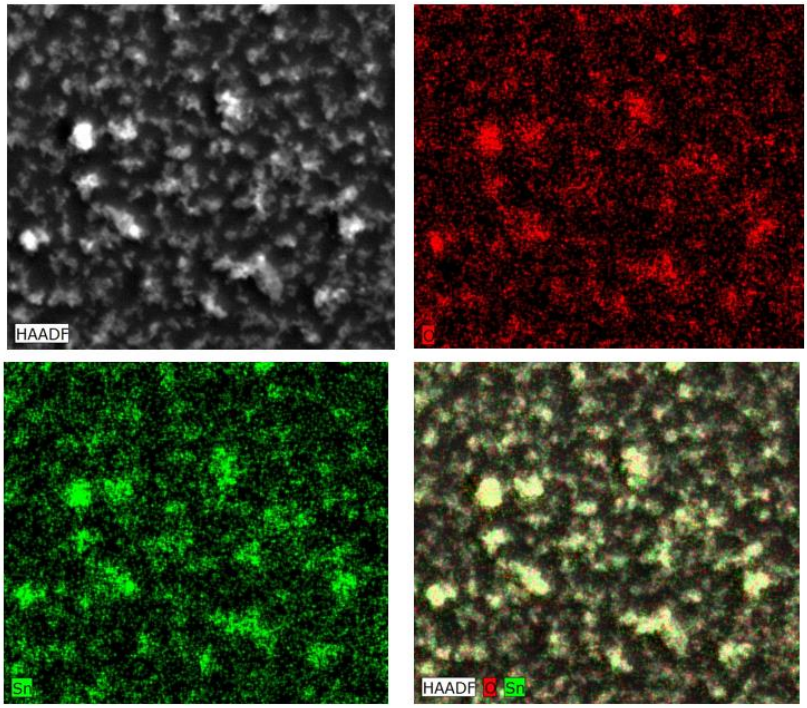

Figure S11 The elemental mapping images of SnO_2 sample.

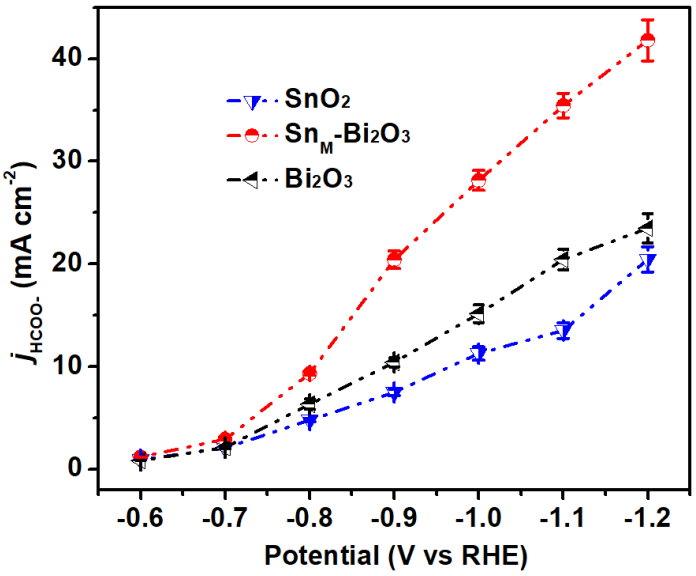

Figure S12 The partial current density of formate at different potential of SnO_2, Sn_M-Bi_2O_3 and Bi_2O_3 catalysts.

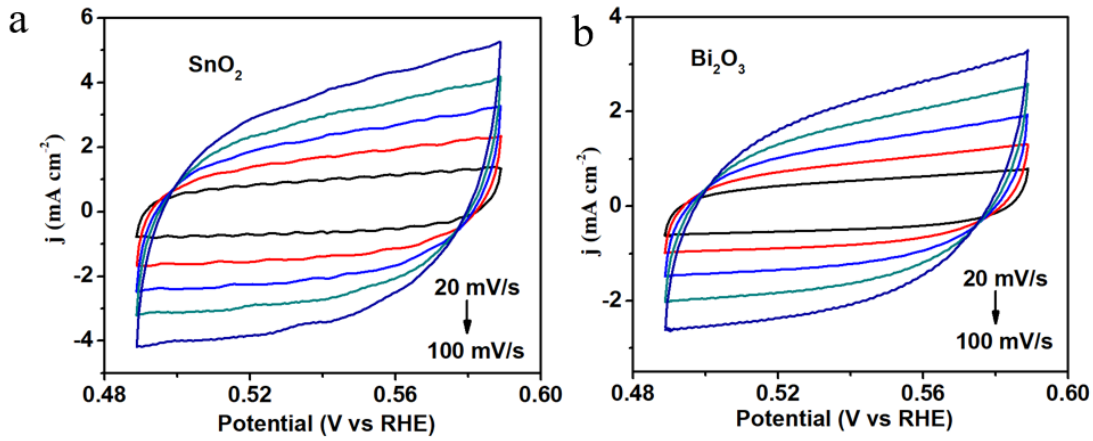

Figure S13 The CV curves vs scan rates for a) SnO_2 and b) Bi_2O_3 catalysts.

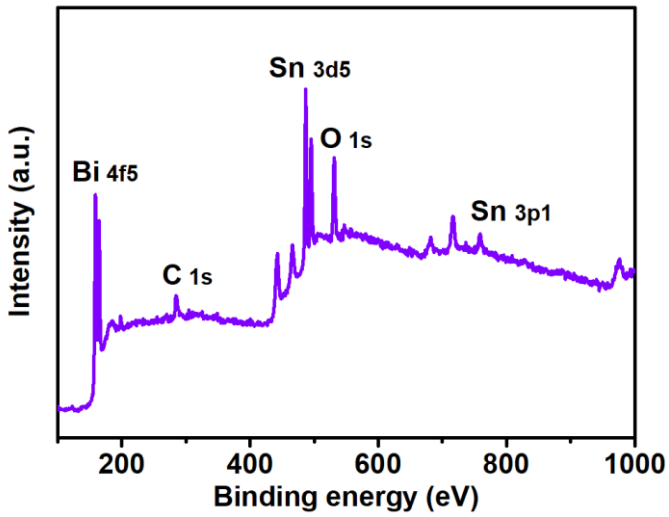

Figure S14 The XPS survey of Sn-Bi_2O_3 catalyst.