Supporting Information

Highly Efficient Electrochemical Reduction of Carbon Dioxide to Formate on Sn Modified Bi₂O₃ Heterostructure

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Experimental Section

The synthesis of Bi₂O₂CO₃ precursor and Bi₂O₃ samples: All chemicals are analytical grade and used without further treatment. In a typical procedure, 2g Bi(NO₃)₂·5H₂O (Sigma, ACS reagent, \(\geq 98.0\%\)) is dissolved into 20 ml dilute HNO₃ solution (1 M) under sonication condition. Then, above solution is gradually dropped into 80 ml of Na₂CO₃ (Sigma, \(\geq 99.0\%\)) 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 °C 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 Bi₂O₃ sample is prepared by annealing the Bi₂O₂CO₃ precursor at furnace under 450 °C in air for 3min. The final yellow samples are taken out and kept for further characterizations.

The synthesis of Sn modified Bi₂O₃ and SnO₂ samples: Typically, 30 mg Bi₂O₃ sample is firstly dispersed in 10 ml acetone solution by sonication treatment. Then, the above solution is heated to 55 °C under constant stirring. Next, different amount of stannous chloride (Aldrich, \(\geq 99.99\%\)) 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 SnL-Bi₂O₃, SnM-Bi₂O₃ and SnH-Bi₂O₃ products, respectively. The simple SnO₂ nanoparticle is prepared by hydrothermal reaction. Typically, 400 mg SnCl₄·5H₂O 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 transferred to autoclave. The reaction is kept for 12 h at 130 °C. 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 (\(\lambda = 1.54178 \text{ Å}\)). 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 KHCO₃ solution. Prior to the measurements, the electrolytes in two compartments are purged with high-pure CO₂ gas for 1 h to reach saturation. All the potentials are converted to reversible hydrogen electrode (RHE) by the equation: \[ E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.197 + 0.0591 \times \text{pH}. \]

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: \[ \text{FEs} = \frac{2F \times n}{Q} = \frac{2F \times n}{(I \times t)}. \]

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$_2$O$_2$CO$_3$ precursor.

Figure S2 The a) XRD pattern and b) TEM image of pristine Bi$_2$O$_3$ sample.
Figure S3 The TEM images of SnL-Bi2O3 and SnH-Bi2O3 samples.

Figure S4 The elemental mapping images of SnL-Bi2O3 product.
Figure S5 The elemental mapping images of SnH-Bi₂O₃ product.
Figure S6 The CV curves vs scan rates for a) SnL-Bi2O3, b) SnM-Bi2O3 and c) SnH-Bi2O3 catalysts. d) The C_{dl} values for SnL-Bi2O3, SnM-Bi2O3 and SnH-Bi2O3 catalysts.
Figure S7 The EIS spectra of Sn\textsubscript{L}-Bi\textsubscript{2}O\textsubscript{3}, Sn\textsubscript{M}-Bi\textsubscript{2}O\textsubscript{3} and Sn\textsubscript{H}-Bi\textsubscript{2}O\textsubscript{3}.

Figure S8 The a) XRD pattern and b) TEM image of Sn\textsubscript{M}-Bi\textsubscript{2}O\textsubscript{3} sample after CO\textsubscript{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$_2$O$_3$ and Bi$_2$O$_3$ catalysts.

Figure S13 The CV curves vs scan rates for a) SnO$_2$ and b) Bi$_2$O$_3$ catalysts.
Figure S14 The XPS survey of Sn-Bi$_2$O$_3$ catalyst.