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

Supporting information

High efficiency electrochemical reduction of CO_2 beyond two-electron transfer pathway on grain boundary rich ultra-small SnO_2 nanoparticles

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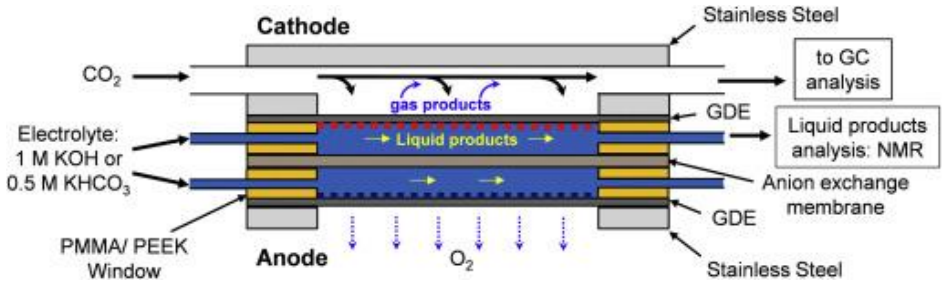

Fig. S1. Schematic of flow cell for CO_2 reduction. (Ref. One-step electrosynthesis of ethylene and ethanol from CO2 in an alkaline electrolyzer)[1]

An electrochemical flow cell reported previously is used as the CO_2 electrolyzer. A schematic of the flow cell used in this study is shown in Fig. S1. In this work, an anion exchange membrane (Fumatech®) is inserted between the catholyte and anolyte chamber to prevent the liquid products from diffusing to the anode where they may get oxidized. Stainless steel plates (5.5 " 2.5 cm) serve as current collectors to hold the flow cell together via a squeeze-action toggle plier clamp (McMaster Carr 5062A63) and provide electrical contact between the GDE and an external potentiostat (Autolab, PGSTAT-30, EcoChemie). Two 1.5-mm thick polyether ether ketone (PEEK) spacers with a precisely machined 0.5-cm wide by 2.0-cm long window provide the catholyte and anolyte flow fields, respectively. The cathode current collector has a precisely machined 0.5-cm wide by 2.0-cm long window with 0.5 cm depth behind the GDE to allow for the flow of gases. The anode is open to air, allowing oxygen to escape.

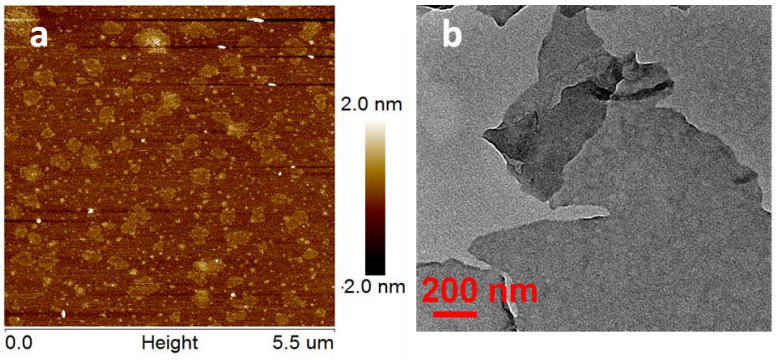

Fig. S2. (a)AFM Picture of SnS_2 Sheets, (b) TEM Picture of SnS_2 Sheets.

The AFM picture of SnS_2 sheets showed the morphology of typical exfoliated 2D materials. The thickness of SnS_2 sheets was in the range of 0.8~1.8nm, indicating the existence of single or few layer SnS_2 sheets. The TEM picture of SnS_2 sheets further confirmed the layer structure.

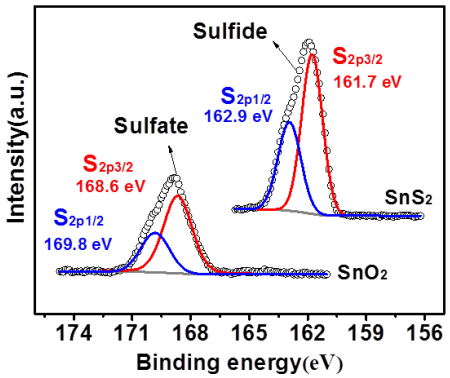

Fig. S3. S_{2p} XPS spectra of SnS_2 sheets and SnO_2 nanoparticles

The S2p XPS spectra shown in Fig. S3 can provide further evidence for the complete transformation from SnS_2 to SnO_2. The S2p XPS spectrum of original SnS_2 nanosheets can be deconvoluted into two peaks at 162.9 eV and 161.7 eV, corresponding to the $2P_{1/2}$ and $2P_{3/2}$ binding energies of SnS_2.When oxidized to SnO_2 nanoparticles, the sulfide was transformed to sulfate chemical structure which shows higher binding energies at 169.8 eV and 168.6 eV for the $2P_{1/2}$ and $2P_{3/2}$ respectively.

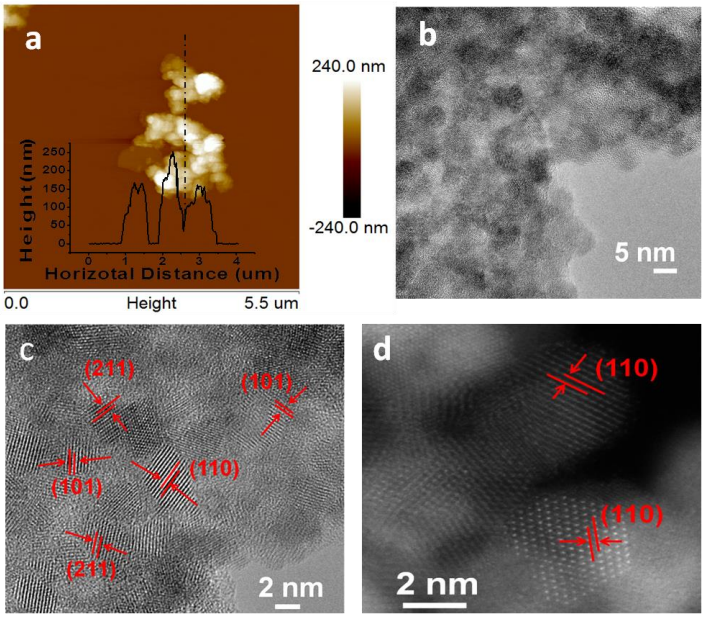

Fig. S4. (a) AFM Picture of SnO_2 nanoparticles, (b)(c)(d)TEM Pictures of SnO_2 nanoparticles.

The AFM picture of SnS_2 sheets after hydrothermal reaction (SnO_2 nanoparticles) showed the morphology of aggregated nanoparticles, which was drastically different from the AFM picture of the original SnS_2 sheets. The corresponding TEM pictures showed the detailed and precise morphology of well-defined nanocrystals with uniform size of about 5nm. In the high magnifications of TEM pictures, measured interplanar spacings of 0.335nm, 0.264nm and 0.176nm corresponding to the (110), (101) and (211) of SnO_2 respectively indicated the chemical nature of nanoparticles to be SnO_2, which was consistent with XRD results.

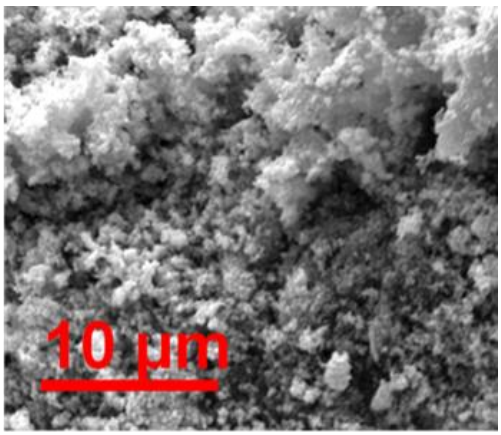

Fig. S5. SEM Pictures of bulk SnO_2(obtained by annealing the bulk SnS_2 at 500°C for 3h in air condition).

The SEM pictures of bulk SnO_2 showed a morphology of aggregated particles with size ranging from 200nm to 500nm. The crystallite size of bulk SnO_2 particles was calculated to be around 28 nm using Debye-Scherrer equation from the XRD result.

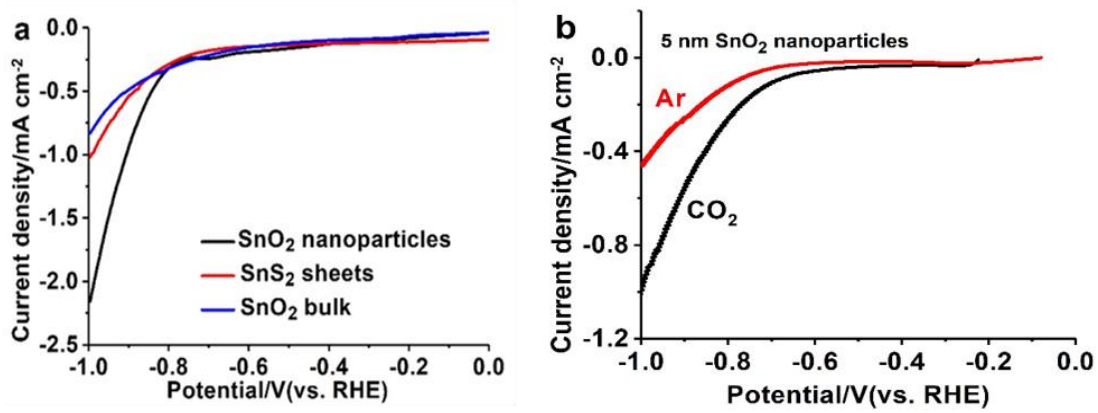

Fig. S6. Linear sweep voltammetric curves in the Ar_2-saturated 1M KOH electrolyte(a) and Ar/CO_2 saturated 0.1 M $KHCO_3$ (b)

The linear sweep voltammetry (LSV) measurement was implemented in a three-electrode system at an potentiostat (Autolab PGSTAT-30, EcoChemie). The working electrode was a glassy carbon electrode. The platinum gauze and the Ag/AgCl electrode served as counter and the reference electrodes, respectively. In a typical prepared procedure of the working electrode, 3 μL of the homogeneous ink, which was prepared by dispersing 5 mg sample and 40 μL Nafion solution (5 wt%) in 1 ml water-ethanol solution with volume ratio of 3:1, was loaded onto a glassy carbon electrode with 3 mm diameter. LSV measurement with a scan rate of 20 mV s^{-1} was carried out in Ar-saturated 1M KOH (60 ml). As revealed by the LSV results shown in Fig.S6, the SnO_2 nanoparticles exhibited the highest current density among the samples, which was roughly 2 and 3 times larger than that of SnS_2 sheets and SnO_2 bulk, respectively, indicating the higher surface area in SnO_2 nanoparticles. The comparison of LSV in Ar_2 and CO_2 saturated 0.1 M $KHCO_3$ shows the typical increasing of current density in CO_2 saturated electrolyte, a potential indicator of CO_2 reduction activity on SnO_2 nanoparticles.

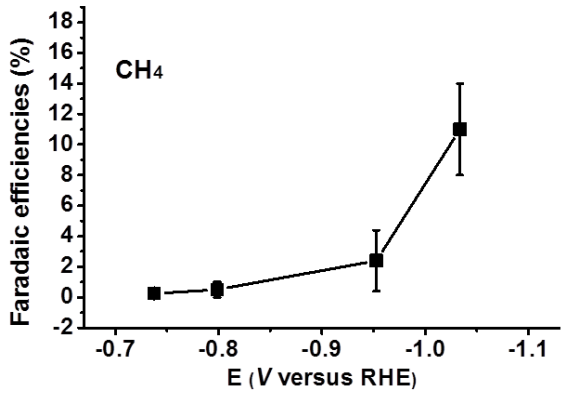

Fig. S7. Faradaic efficiencies for CH_4 formation on SnO_2 nanoparticle electrode in 1M KOH electrolyte.

The noticeable average amounts of 2% CH_4 and 11% CH_4 detected at applied potentials of -0.95V and -1.03V respectively, shown Fig. S7 should be emphasized

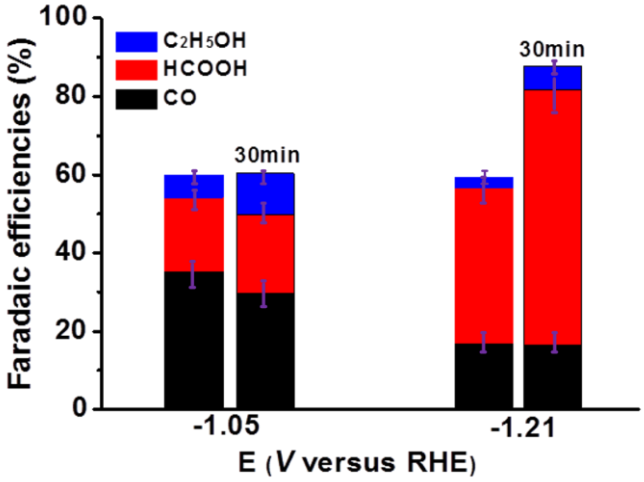

Fig. S8. Faradaic efficiencies for CO_2 reduction on SnO_2 nanoparticle electrode tested in 1M $KHCO_3$ electrolyte before and after 30min electrolysis in the electrolyte, respectively.

It is interesting to find that when the SnO_2 nanoparticle catalyst was tested in the electrolyte of $KHCO_3$, C_2H_5OH showed a higher selectivity over CH_4, reaching a FE of 5.8% at -1.05V aside from the main products of CO (FE of 35.3%) and HCOO- (FE of 18.8%) as shown in Fig. S8. While the applied potential was more negative(-1.21 V), a higher FE of HCOO- (39.6%) was achieved. After the SnO_2 nanoparticle catalyst was under electrolysis for 30 min, the FE of C_2H_5OH increased from 5.8% to 10.4% at -1.05V, from 2.5% to 6.0% at -1.21V, possibly due to the component change in the metastable SnO_X/Sn layer after electrolysis under reduction potentials for 30 min.

References

[1] S. Ma, M. Sadakiyo, R. Luo, M. Heima, M. Yamauchi, P.J.A. Kenis, One-step electrosynthesis of ethylene and ethanol from CO2 in an alkaline electrolyzer, J. Power Sources, 301 (2016) 219-228.