Electronic Supplementary Information

Synthesis of Sn$_4$P$_3$/Reduced Graphene Oxide Nanocomposites as Highly Efficient Electrocatalysts for CO$_2$ Reduction

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Experimental Procedures

Reagents

$SnCl_2 \cdot 2H_2O$ (purity>99.9%) were provided by Sinopharm Chem. Reagent Co. Ltd. Ethylenediamine (purity>99%) and $NaBH_4$ (A. R. grade) were purchased from Beijing Chemical Company. Red phosphorus (purity>99%), Toray Carbon Paper (CP, TGP-H-60, 19×19 cm), Nafion N-117 membrane (0.180 mm thick, ≥ 0.90 meg/g exchange capacity) and Nafion D-521 dispersion (5 % w/w in water and 1-propanol, ≥ 0.92 meg/g exchange capacity) were purchased from Alfa Aesar China Co., Ltd. PVP and citric acid (purity>99%) was purchased from J&K. Graphene oxide (GO) was obtained from Institute of Coal Chemistry, Chinese Academy of Sciences. 1-Butyl-3-methylimidazolium hexafluorophosphate ([Bmim]PF_6, purity>99%) was provided by the Centre of Green Chemistry and Catalysis, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences.

Synthesis of the Sn_4P_3/RGO nanocomposites

In a typical synthesis of Sn/RGO nanocomposite, PVP (0.1 g) and citric acid (0.1 g) were dissolved in 30 mL de-ionized water under ultrasonication. Then, 10 mL GO suspension (4 mg mL^{-1}) was added into above solution to form solution A. 20 mL of freshly prepared $SnCl_2 \cdot 2H_2O$ (0.2 g) under ultrasonication was added into solution A drop by drop under stirring for 1 h. Next, 20 mL of freshly prepared $NaBH_4$ (90 mg) aqueous solution was quickly added under the purging of N_2 as a protecting gas. The color of the solution turned to black immediately. The resulting solution was kept stirring for 1 h. The resultant black products were separated by centrifugation (10000 rpm for 5 min) and washed several times with ultrapure water (5 × 30 mL) and ethanol (5 × 30 mL) to remove impurities. Finally, Sn/RGO nanocomposite was dried in a vacuum oven at 60 °C for 6 h. 81.1-Sn_4P_3/RGO was obtained by the addition of 1.2 g Sn/RGO and 0.464 g red phosphorus into 60 mL ethylenediamine solution and kept stirring for 12 h. The mixture was transferred into an 80 mL Teflon-lined stainless-steel autoclave and put into the muffle furnace at 200 °C for 40 h. The system was cooled to ambient temperature naturally and washed several times with ultrapure water (5 × 30 mL) and ethanol (5 × 30 mL), then dried in a vacuum oven at 60 °C for 6 h. The ratio of the Sn/RGO nanocomposites can be controlled by tuning the ratio of $SnCl_2 \cdot 2H_2O$ and GO. The prepared samples were denoted as 34.2-Sn_4P_3/RGO, 55.2-Sn_4P_3/RGO, 69.9-Sn_4P_3/RGO and 88.3-Sn_4P_3/RGO for 80, 40, 20, 10 mL graphene oxide suspension (4 mg mL^{-1}).

Materials characterization

The morphologies of Sn_4P_3/RGO were characterized by a JEOL-2100F TEM operated at 200 kV. The content of metal in the catalysts was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES, Vista-MPX). X-ray photoelectron spectroscopy (XPS) analysis was performed on the Thermo Scientific ESCA Lab 250Xi using 200 W monochromatic Al Kα radiation. The 500 μm X-ray spot was used for the XPS analysis. The base pressure in the analysis chamber was about 3×10^{-10} mbar. Typically, the hydrocarbon C1s line at 284.8 eV from adventitious carbon is used for energy referencing. Powder X-ray diffraction (XRD) patterns were collected on the X-ray diffractometer (Model D/MAX2500, Rigaka) with Cu-Kα radiation. Thermogravimetric (TG) measurements were conducted using a TGA4000 analyzer from 30 ℃ to 700 ℃ with a heating rate of 10 ℃ min^{-1} under a N_2 flow of 60 mL min^{-1} with open alumina pans. The Raman spectra of the Sn_4P_3-RGO samples were obtained at room temperature in flame-sealed capillary on a FT Bruker RFS 106/S spectrometer, equipped with a 514 nm laser, in the region from 4000 to 100 cm^{-1} with a resolution of 2 cm^{-1}.

Electrochemical study and product analysis

The electrochemical workstation (CHI 660E, Shanghai CH Instruments Co., China) was used for all CO_2 reduction experiments. Linear sweep voltammetry (LSV) measurements were performed in a single compartment batch cell with a typical three-electrode setup, which contained working electrode (catalyst dropped on carbon paper), a platinum gauze auxiliary electrode, and an Ag/Ag^+ (0.01 M $AgNO_3$ in 0.1 M TBAP-MeCN) reference electrode. Before electrolysis, the electrolyte was purged with N_2 or CO_2 gas for at least 20 min.

The LSV measurement in gas-saturated electrolyte was conducted at a sweep rate of 20 mV/s in the potential between -1.8 V and -2.6 V (vs. Ag/Ag^+). Constant magnetic stirring was kept in the process. The electrolysis experiments were conducted at 25 °C in a typical H-type cell which was similar to that used in our previous work.[1] In the experiments, the cathode and anode compartments were separated by a Nafion 117 proton exchange membrane. H_2SO_4 aqueous solution (0.5 M) was used as anodic electrolyte. H^+ could be transferred from anode compartment to cathode compartment through Nafion 117 proton exchange membrane. Under the continuous stirring, CO_2 flowed through the catholyte for 15 min before electrolysis. Then, potentiostatic electrochemical reduction of CO_2 was carried out with CO_2 bubbling (2 mL/min).

The liquid product was analyzed by ^1H NMR (Bruker Avance III 400 HD spectrometer) in dimethyl sulfoxide-d_6 with TMS as an internal standard. The gaseous product of electrochemical experiments was collected by using a gas bag and analyzed by gas chromatography (GC, HP 4890D).

Electrochemical impedance spectroscopic (EIS) studies were performed in the frequency range from 0.1 to 100,000 Hz and amplitude of 5 mV.

Calculations of Faradaic efficiencies of the gas products:[2]

FE = moles of products per second / theoretical moles equivalent per second
From the GC peak areas and calibration curves for the TCD detector, we can obtain the V % of H_2. Since the flow rate of the gas was known, the amount of moles of H_2 (or CO) per second could be calculated. The theoretical moles per second were obtained from current density since production of H_2 (or CO) proceeded via 2-electron paths.

Table S1. The CO_2 electrocatalytic reduction over different Sn based electrodes in different electrolytes.

Electrode/ electrocatalysts	Electrode potential / V	Electrolyte	Product and FE / %	CD / mA cm^{-2}	Ref.
81.1-Sn$_4$P$_3$/RGO nanocomposite	-2.4 V vs Ag/Ag$^+$	MeCN contain 0.5 M [Bmim]PF$_6$	CO / 96.6	68	This work
Ultrafine nanoscale tin oxide	-1.8 V vs. SCE	0.1 M NaHCO$_3$	formate / 93.6	>10	3
ultrathin Sn quantum sheets layers confined in graphene	-1.8 V vs. SCE	0.1 M NaHCO$_3$	formate / 90	21.1	4
Sn/SnS$_2$ derived from SnS$_2$ nanosheets	-1.4 V vs Ag/AgCl	0.5 M NaHCO$_3$	Formate / 84.5	13.9	5
SnO$_x$	-0.7 V vs RHE	0.5 M NaHCO$_3$	>85 CO_2 reduction	1.8	6
Ag−Sn Bimetallic	-0.8 V vs RHE	0.5 M NaHCO$_3$	Formate / 80	16	7
Core/Shell Cu/SnO$_2$ Structure	-0.7 V vs RHE	0.5 M KHCO$_3$	CO 93	Not giving	8
SnO Nanoparticles	-0.66 V vs RHE	0.5 M KHCO$_3$	CO 30 -40	13	9
SnO$_2$ Porous Nanowires	-0.8 V vs RHE	0.1 M KHCO$_3$	HCOOH 80	10	10
electrodeposited SnO$_2$@N-doped porous carbon	-2.2 V vs Ag/Ag$^+$	MeCN contain 0.5 M [Bmim]PF$_6$	HCOOH / 94.1	28.4	11
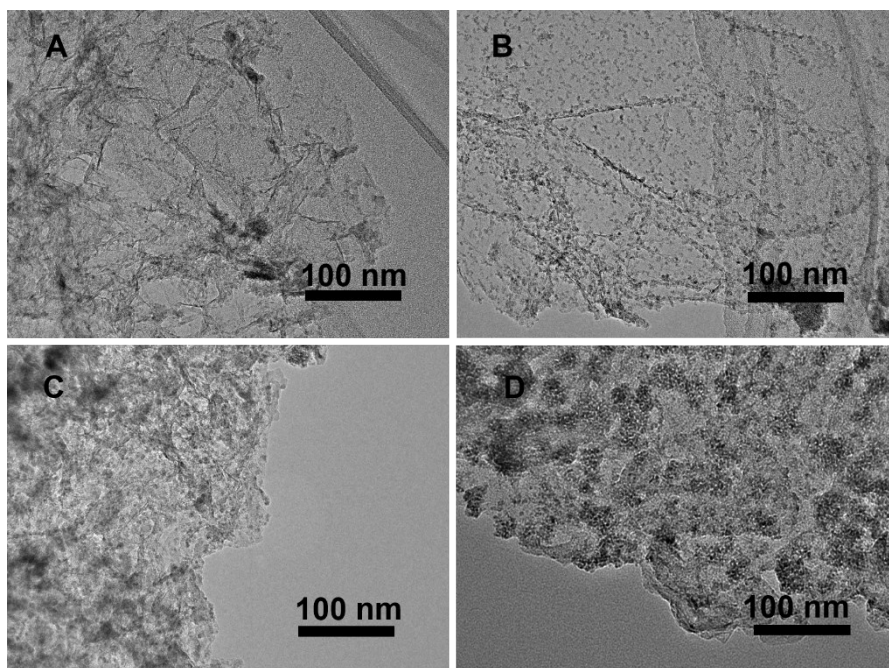
Figure S1. TEM images of (A) 34.2-Sn_4P_3/RGO, (B) 55.2-Sn_4P_3/RGO, (C) 69.9-Sn_4P_3/RGO and (D) 88.3-Sn_4P_3/RGO.
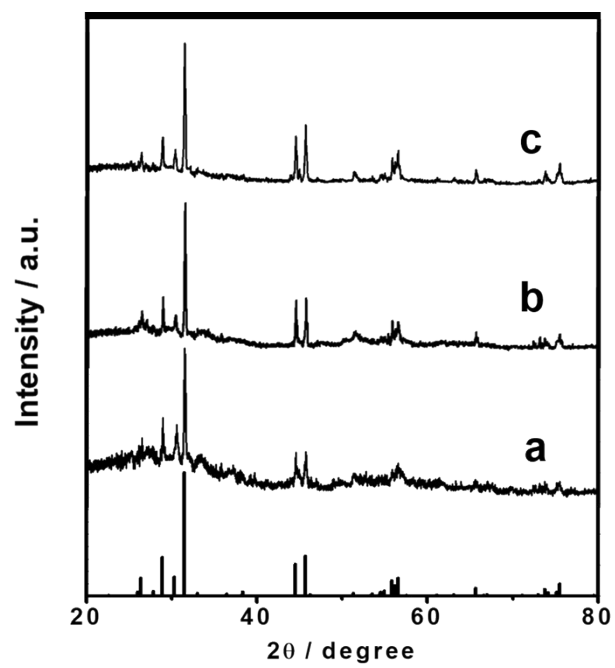
Figure S2. XRD patterns of of (a) 34.2-Sn_4P_3/RGO, (b) 55.2-Sn_4P_3/RGO, (c) 69.9-Sn_4P_3/RGO.
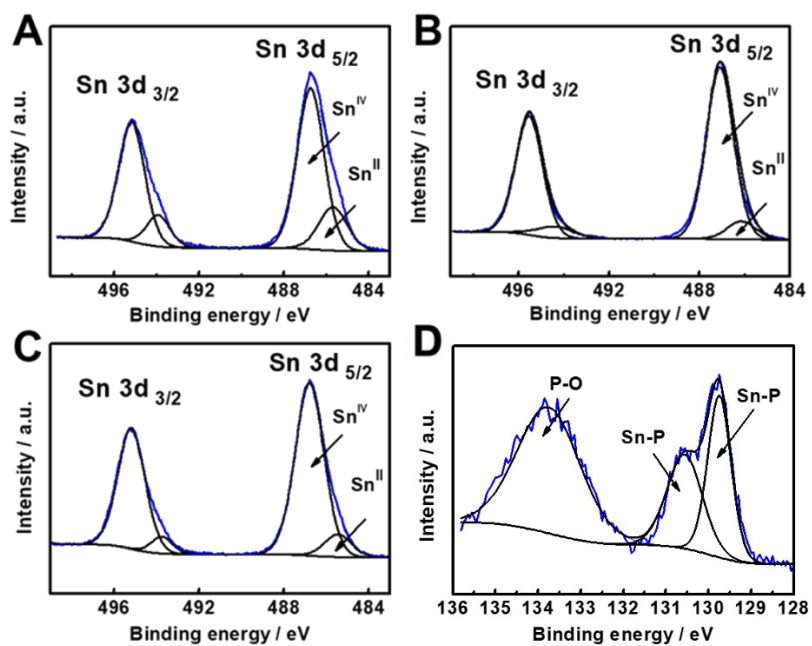
Figure S3. XPS spectra of Sn in (A) 34.2-Sn_4P_3/RGO, (B) 55.2-Sn_4P_3/RGO, (C) 69.9-Sn_4P_3/RGO and (D) P in 81.1-Sn_4P_3/RGO.
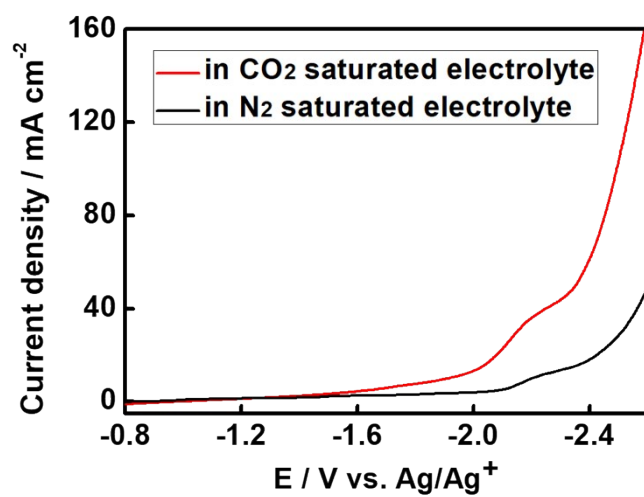
Figure S4. LSV curves for 81.1-Sn_4P_3/RGO in N_2-saturated and CO_2-saturated MeCN containing 0.5 M [Bmim]PF_6.
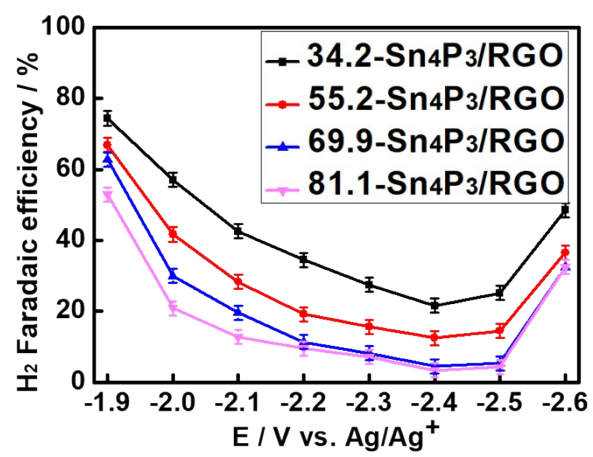
Figure S5. Faradaic efficiency for H_2 over Sn_4P_3/RGO samples.
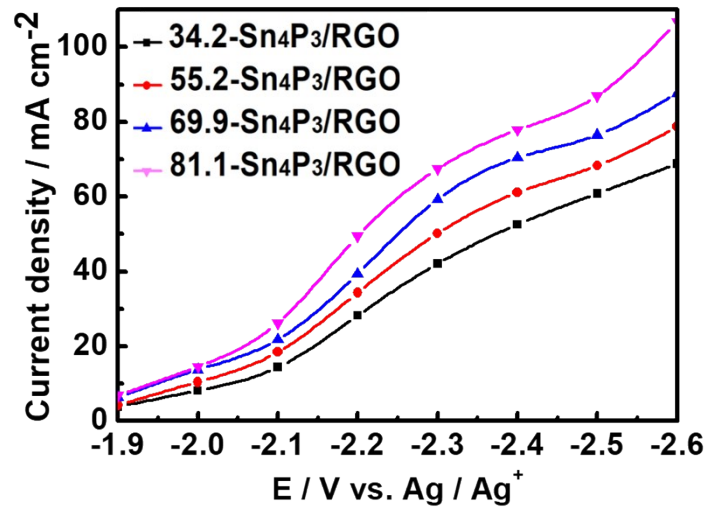
Figure S6.The total current density for 34.2-Sn_4P_3/RGO, 55.2-Sn_4P_3/RGO, 69.9-Sn_4P_3/RGO and 81.1-Sn_4P_3/RGO electrodes in CO_2-saturated MeCN containing 0.5 M [Bmim]PF_6 electrolyte at different applied potentials.
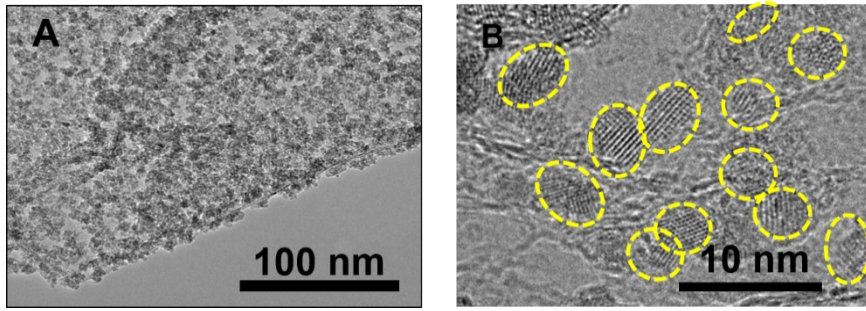
Figure S7.(A) TEM and (B) HR-TEM images of 81.1-Sn$_4$P$_3$/RGO after 12 h electrolysis.
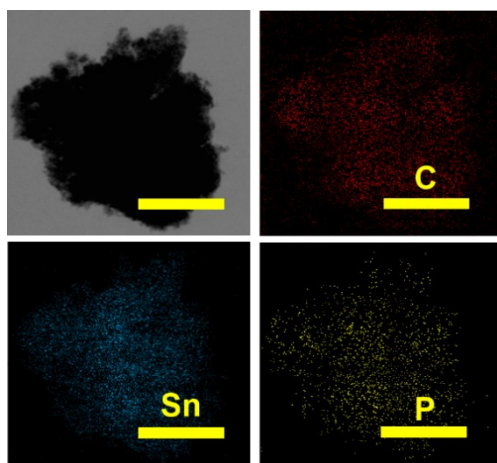
Figure S8. EDX mapping images (scale bar: 200 nm) of 81.1-Sn_4P_3/RGO after 12 h electrolysis.

References

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