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Electronic Supplementary Information (ESI)

Rethinking $Co(CO_3)_{0.5}(OH)\cdot 0.11H_2O$: New property for highly selective electrochemical reduction of carbon dioxide to methanol in aqueous solution

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Experimental details

Chemicals and reagents: Cobalt(III) acetylacetonate (98%, analytical grade), dimethylformamide (99.8%, analytical grade) and dimethyl sulfoxide (DMSO, 99.9%, analytical grade) were purchased from J&K Chemical (Beijing, China). *n*-butylamine (99%, analytical grade) was obtained from TCI Company. 5 wt% Nafion perfluorinated resin solution was obtained from Sigma-Aldrich Chemical Co. (St. Louis, MO, USA). High purity carbon dioxide (≥99.999%) was purchased from Guangzhou Shengying Gas Co., Ltd. All other reagents were of analytical grade and used without further purification, the purity of the salt used in different aqueous solutions ≥ 99.9%, all aqueous solutions were prepared with doubly distilled water.

Synthesis of hollow urchin-like $Co(CO_3)_{0.5}(OH)\cdot 0.11H_2O$: 62.5 mg cobalt(III) acetylacetonate was added into a solution of 12.5 mL dimethylformamide, 2.5 mL H_2O and 0.625 mL *n*-butylamine. After vigorous stirring for 15 min, the mixture was transferred into a 25-mL Teflon autoclave, heated at 220 °C for 3 h. Finally, the autoclave was cooled down to room temperature, and the product was collected by centrifuging the mixture (washed with cyclohexane and absolute ethanol), then dried in vacuum.

Synthesis of solid flower-like $Co(CO_3)_{0.5}(OH)\cdot 0.11H_2O$: 6 mg cobalt(III) acetylacetonate was added into a solution of 10 mL dimethylformamide, 1 mL H_2O and 1 mL *n*-butylamine. After vigorous stirring for 15 min, the mixture was transferred into a 25-mL Teflon autoclave, heated at 220 °C for 2 h. Finally, the autoclave was cooled down to room temperature, and the product was collected by centrifuging the mixture (washed with cyclohexane and absolute ethanol), then dried in vacuum.

Synthesis of Co sphere: 62.5 mg cobalt(III) acetylacetonate was added into a solution of 12.5 mL dimethylformamide, 2.5 mL H_2O and 1.25 mL *n*-butylamine. After vigorous stirring for 15 min, the mixture was transferred into a 25-mL Teflon autoclave, heated at 220 °C for 48 h. Finally, the autoclave was cooled down to room temperature, and the product was collected by centrifuging the mixture (washed with cyclohexane and absolute ethanol), then dried in vacuum.

Synthesis of hollow urchin-like Co_3O_4: 62.5 mg cobalt(III) acetylacetonate was added into a solution of 12.5 mL dimethylformamide, 2.5 mL H_2O and 0.625 mL *n*-butylamine. After vigorous stirring for 15 min, the mixture was transferred into a 25-mL Teflon autoclave, heated at 220 °C for 3 h. Finally, the autoclave was cooled down to room temperature, and the product was collected by centrifuging the mixture (washed with cyclohexane and absolute ethanol), then dried in vacuum. The obtained hollow urchin-like $Co(CO_3)_{0.5}(OH)\cdot 0.11H_2O$ precursor was annealed under air atmosphere, following a 3 °C/min ramp to 350 °C, and the annealing was maintained at 350 °C for 2 h, and then naturally cooled to room temperature. Finally, the hollow urchin-like Co_3O_4 was obtained.

Electrochemical measurements and product analysis: The electrochemical measurements were performed on a conventional three-electrode system at CHI 660D electrochemical workstation (Chenhua, Shanghai, China), in which saturated calomel electrode (SCE) as reference electrode and platinum wire as counter electrode. All of the potentials in this work were with respect to SCE, and the relationship between SCE and reversible hydrogen electrode (RHE) was shown in following equation: $E(vs.\ SCE) = E(vs.\ RHE) - 0.059 \times pH - 0.241\ (V)$.[1,2] The working electrode was fabricated through loading sample suspension onto the glassy carbon electrode. Firstly, 5 mg hollow urchin-like $Co(CO_3)_{0.5}(OH)\cdot 0.11H_2O$ electrocatalyst was dispersed in 5 mL water and sonicated for 15 min to form a 1 mg mL^{-1} homogeneous suspension. Then, 5 μL of the well dispersed catalyst suspension was loaded onto the pre-polished 3 mm glassy carbon electrode, which gives the loading of electrocatalyst was about 5 μg. After drying under infrared lamp, 10 μL of 0.445 wt% Nafion solution (1 mL 5 wt% Nafion solution + 5 mL H_2O + 5 mL absolute ethanol) was dropped onto the surface of the catalyst layer to form a thin protective film, and then dried under infrared lamp. For carbon dioxide electrochemical reduction experiments, the electrolytes were all purged with CO_2 for 30 min to saturate prior to the measurement, constant-potential electrolysis and linear sweep voltammetry (LSV) with a scan rate of 20 mV s^{-1} were carried out in 25 mL CO_2-saturated 0.1 M $NaHCO_3$ (pH=6.7), 0.1 M NaCl (pH=3.9), 0.1 M Na_2SO_4 (pH=4.3) and 0.1 M $NaNO_3$ (pH=4.1) aqueous solutions. The liquid products were quantified by NMR spectroscopy, in which 0.5 mL electrolyte was mixed with 0.1 mL D_2O (deuterated water) and 0.5 μL dimethyl sulfoxide (DMSO), DMSO was added as an internal standard. A gas chromatograph (GC, Varian 3800 GC) equipped with PLOT MolSieve 5A and Q-bond PLOT columns was used for quantification of gas-phase products. Gas-phase products were sampled every 30 min using a gas-tight syringe (Hamilton), Helium (99.999%) was used as the carrier gas. The separated gas products were analyzed by a thermal conductivity detector (for H_2) and a flame ionization detector (for CO and hydrocarbons). Electrochemical surface area (ECSA) was measured according to previous work[3] based on equation: ECSA = $R_f S$. Faradaic efficiency of methanol (η_{methanol}) was calculated from the total amount of charge Q (in units of coulombs) passed through the sample and the total amount of methanol produced n_{methanol} (in moles).[3] Six electrons are required to produce one methanol molecule, the Faradaic efficiency can be calculated as follows: Faradaic efficiency = $6F \times n_{\mathrm{methanol}}/Q$, where F is the Faraday constant.

Physical characterizations: X-ray diffraction (XRD) patterns were recorded on a Bruker D4 X-ray diffractometer (Germany). X-ray photoelectron spectroscopy (XPS) was performed on ESCALAB 250Xi (Thermo Scientific, America), the binding energies obtained in the XPS spectral analysis were corrected for specimen charging by referencing C 1s to 284.8 eV.[4] The surface morphology was characterized using a field emission scanning electron microscope (FE-SEM; Zeiss Ultra55, Germany). Transmission electron microscopy (TEM) with Energy Dispersive X-Ray Spectroscopy (EDS) measurements were conducted on JEOL-2100F microscope (Japan). Raman spectra were acquired using a LabRAM Aramis spectrometer equipped with a He-Ne (633 nm) excitation source (Horiba Jobin-Yvon, France). Nitrogen sorption isotherm of Brunauer-Emmett-Teller (BET) method was measured at 77 K with a Micromeritcs Tristar 3000 analyzer (USA). ^1H and ^{13}C nuclear magnetic resonance (NMR) was recorded on a Bruker AVANCE AV III 400 spectroscopy.

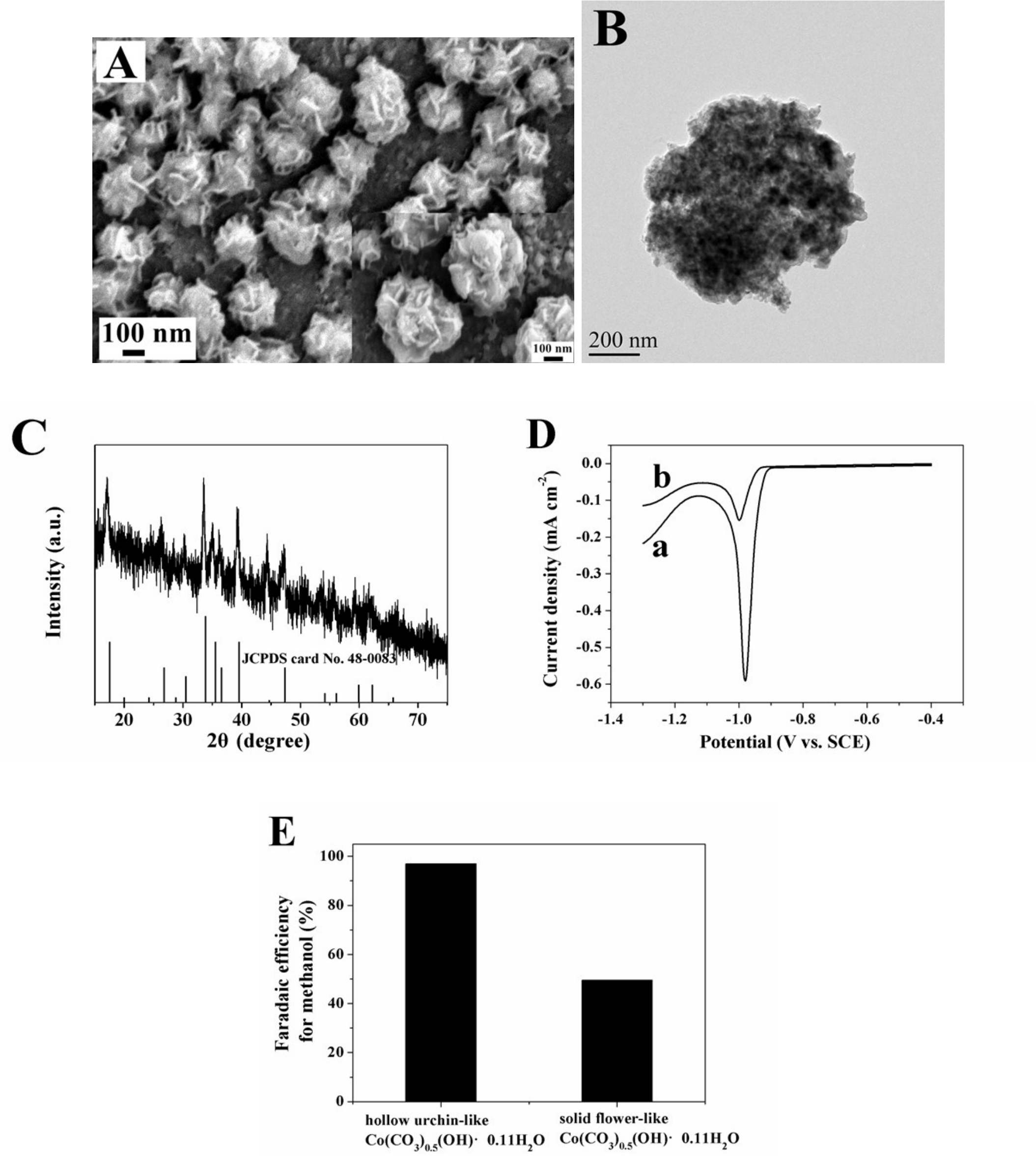

Fig. S1 (A) SEM image, (B) TEM image and (C) XRD pattern of solid flower-like $Co(CO_3)_{0.5}(OH)\cdot 0.11H_2O$. (D) Linear sweep voltammograms of (a) hollow urchin-like $Co(CO_3)_{0.5}(OH)\cdot 0.11H_2O$ and (b) solid flower-like $Co(CO_3)_{0.5}(OH)\cdot 0.11H_2O$ in CO_2-saturated 0.1 M $NaHCO_3$ aqueous solution (scan rate of 20 mV s^{-1}). (E) Faradaic efficiency of methanol obtained from electrochemical reduction of CO_2 at −0.98 V (vs. SCE) for 10 h.

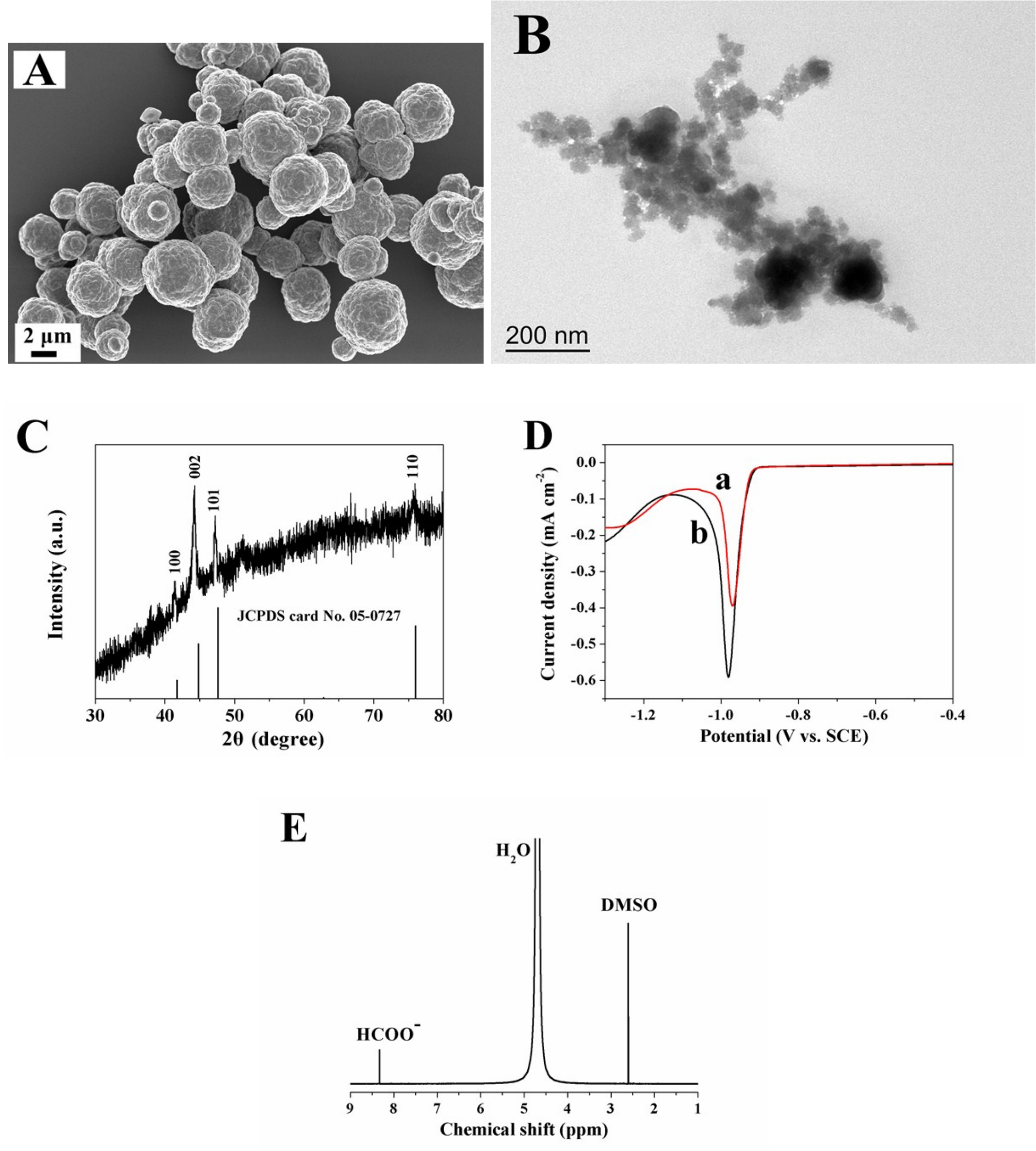

Fig. S2 (A) SEM image, (B) TEM image and (C) XRD pattern of Co sphere. (D) Linear sweep voltammograms of (a) Co sphere and (b) hollow urchin-like $Co(CO_3)_{0.5}(OH)\cdot 0.11H_2O$ in CO_2-saturated 0.1 M $NaHCO_3$ aqueous solution (scan rate of 20 mV s^{-1}). (E) ^1H-NMR spectra of the electrolyte after CO_2 reduction electrolysis at −0.98 V (vs. SCE) for 10 h at the Co sphere.

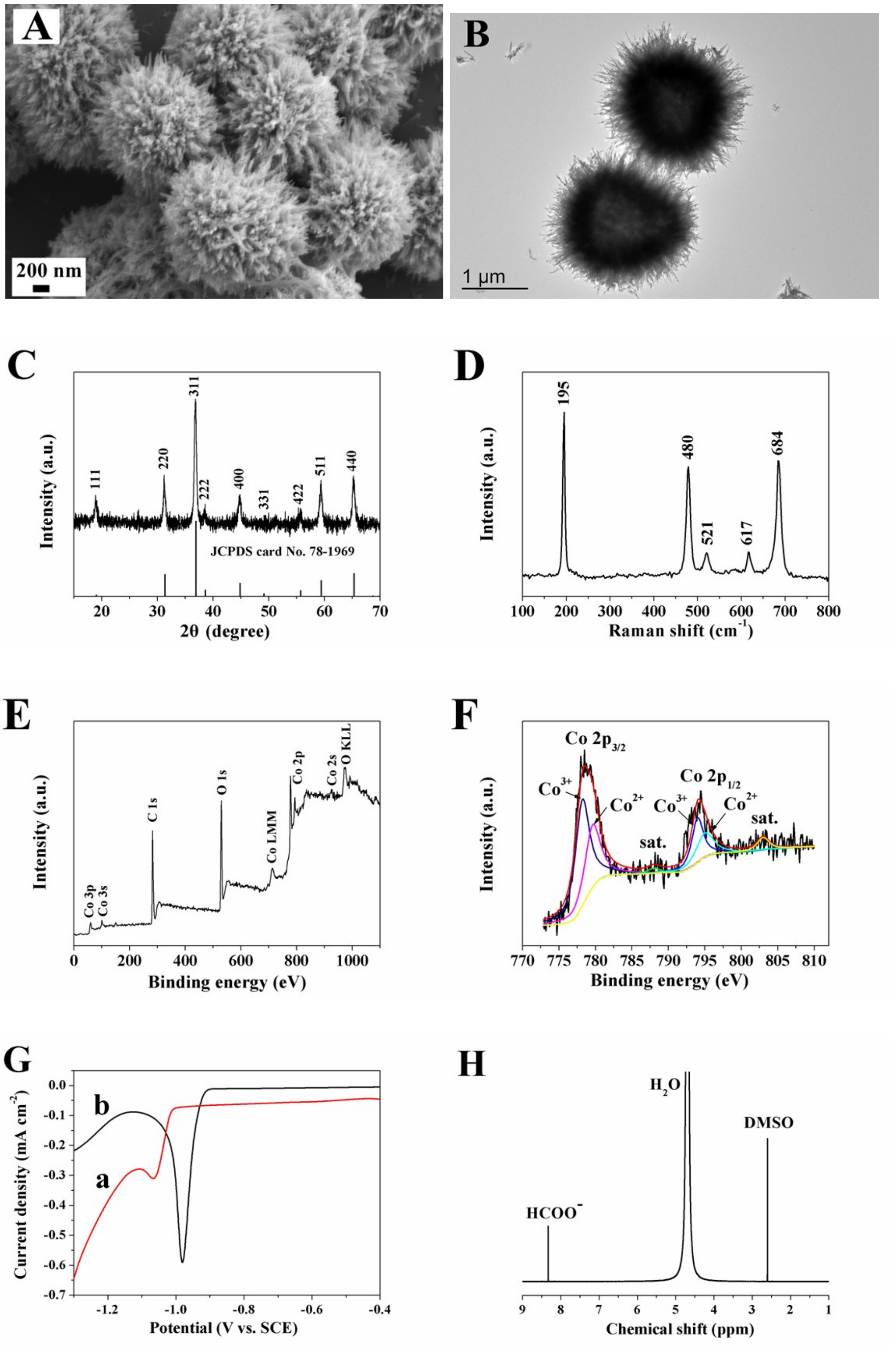

Fig. S3 (A) SEM image, (B) TEM image, (C) XRD pattern, (D) Raman spectrum, (E) Survey XPS spectrum and (F) high resolution Co 2p XPS spectrum of hollow urchin-like Co_3O_4. (G) Linear sweep voltammograms of (a) hollow urchin-like Co_3O_4 and (b) hollow urchin-like $Co(CO_3)_{0.5}(OH)\cdot 0.11H_2O$ in CO_2-saturated 0.1 M $NaHCO_3$ aqueous solution (scan rate of 20 mV s^{-1}). (H) ^{1}H-NMR spectra of the electrolyte after CO_2 reduction electrolysis at −1.06 V (vs. SCE) for 10 h at the hollow urchin-like Co_3O_4.

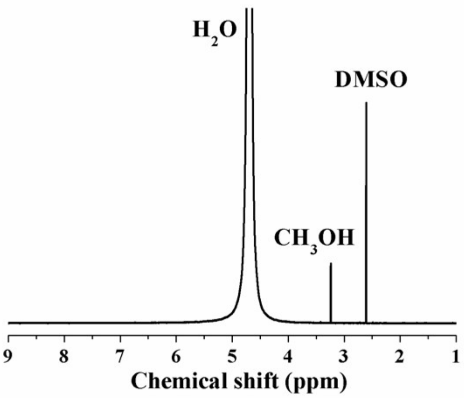

Fig. S4 ^{1}H-NMR spectra of the electrolyte after CO_2 reduction electrolysis at −0.98 V (vs. SCE) for 10 h at Cu electrode.

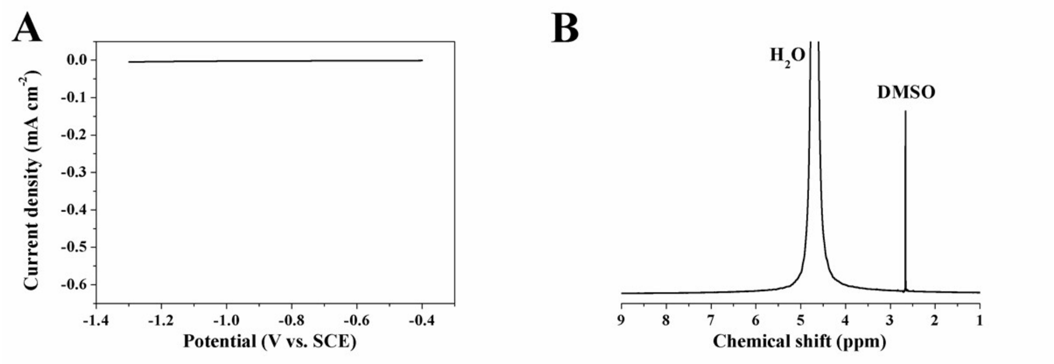

Fig. S5 (A) Linear sweep voltammogram of bare glassy carbon electrode in CO_2-saturated 0.1 M $NaHCO_3$ aqueous solution (scan rate of 20 mV s^{-1}). (B) ^{1}H-NMR spectra of the electrolyte after CO_2 reduction electrolysis at −0.98 V (vs. SCE) for 10 h at bare glassy carbon electrode.

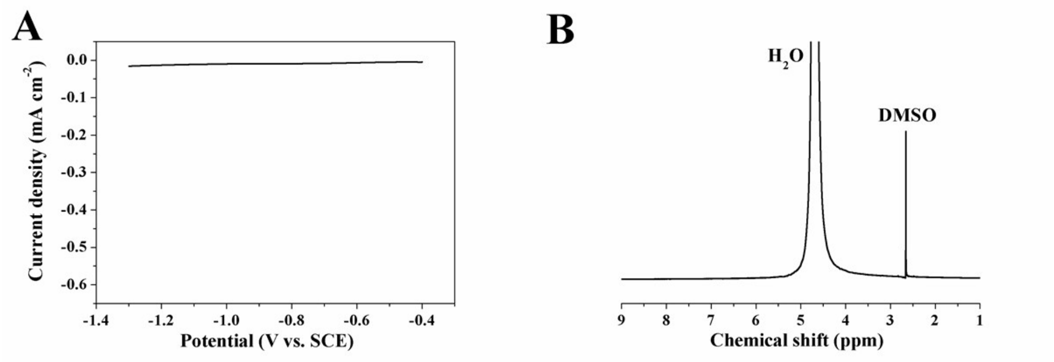

Fig. S6 (A) Linear sweep voltammogram of bare glassy carbon electrode with Nafion film in CO_2-saturated 0.1 M $NaHCO_3$ aqueous solution (scan rate of 20 mV s^{-1}). (B) ^{1}H-NMR spectra of the electrolyte after CO_2 reduction electrolysis at −0.98 V (vs. SCE) for 10 h at bare glassy carbon electrode with Nafion film.

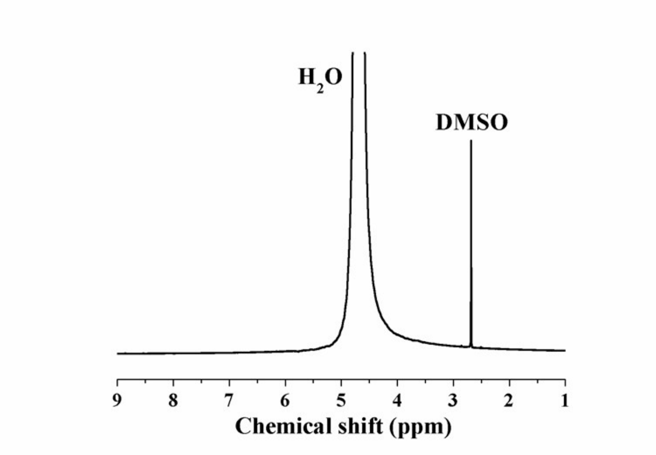

Fig. S7 ^{1}H-NMR spectra of the electrolyte after electrolysis in N_2-saturated 0.1 M $NaHCO_3$ aqueous solution at −0.98 V (vs. SCE) for 10 h at hollow urchin-like $Co(CO_3)_{0.5}(OH)\cdot 0.11H_2O$.

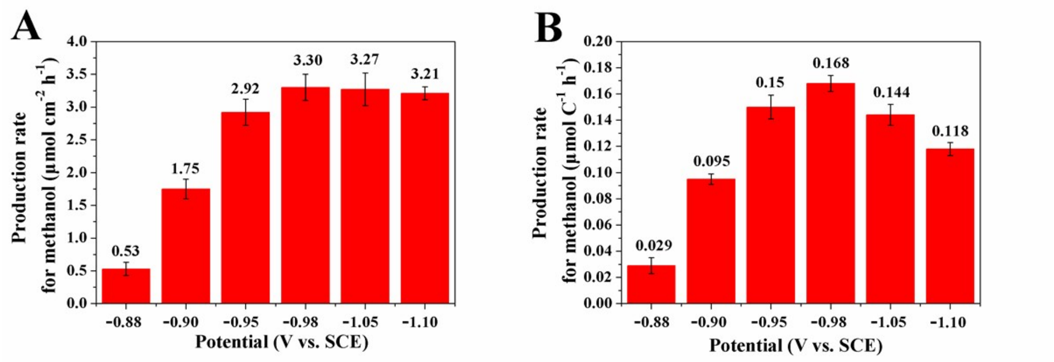

Fig. S8 Production rates of methanol normalized by (A) available reaction area and (B) charge obtained from electrochemical reduction of CO_2 for 10 h at hollow urchin-like $Co(CO_3)_{0.5}(OH)\cdot 0.11H_2O$ under different applied electrolysis potentials.

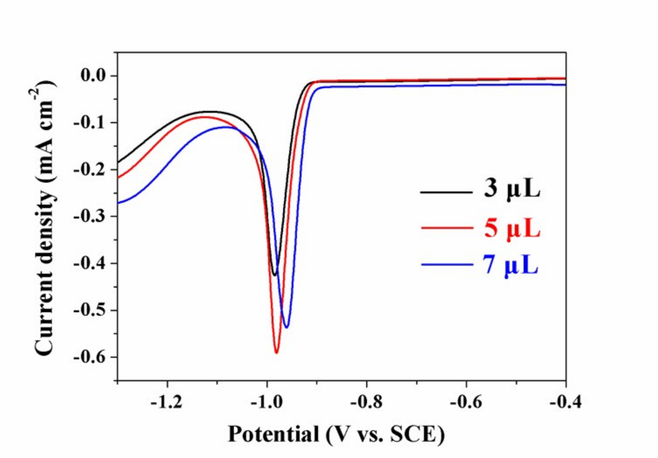

Fig. S9 Linear sweep voltammograms of 3 μL, 5 μL and 7 μL of 1 mg mL^{-1} hollow urchin-like $Co(CO_3)_{0.5}(OH)\cdot 0.11H_2O$ in CO_2-saturated 0.1 M $NaHCO_3$ aqueous solution (scan rate of 20 mV s^{-1}).

Table S1 Comparison of the production rate and faradaic efficiency for methanol among prepared hollow urchin-like $Co(CO_3)_{0.5}(OH)\cdot 0.11H_2O$ catalysts and other materials reported in the literature.

Catalysts	Electrolyte	Experimental conditions	Production rates	Faradaic efficiency	Ref.
Oxide-derived Cu/C	0.1 M $KHCO_3$	−0.94 V (SCE)	12.4 mg L^{-1} h^{-1}	43.2%	2
Cu-Au alloy	0.5 M $KHCO_3$	−1.1 V (SCE)	Not reported	15.9%	5
RuO_2/TiO_2 nanotubes	0.5 M $NaHCO_3$	–0.8 V (SCE)	Not reported	60.5%	6
Electrodeposited cuprous oxide electrodes	0.5 M $KHCO_3$	−1.1 V (SCE)	43 μmol cm^{-2} h^{-1}	38%	7
$Cu_{88}Sn_6Pb_6$ alloy	2 M HCl solution	−0.70 V (SCE)	1.8×10^{-5} mol m^{-2} s^{-1}	36.3%	8
Hollow urchin-like $Co(CO_3)_{0.5}(OH)\cdot 0.11H_2O$	0.1 M $NaHCO_3$	−0.98 V (SCE)	145.0 mmol g^{-1} h^{-1}	97.0%	This work

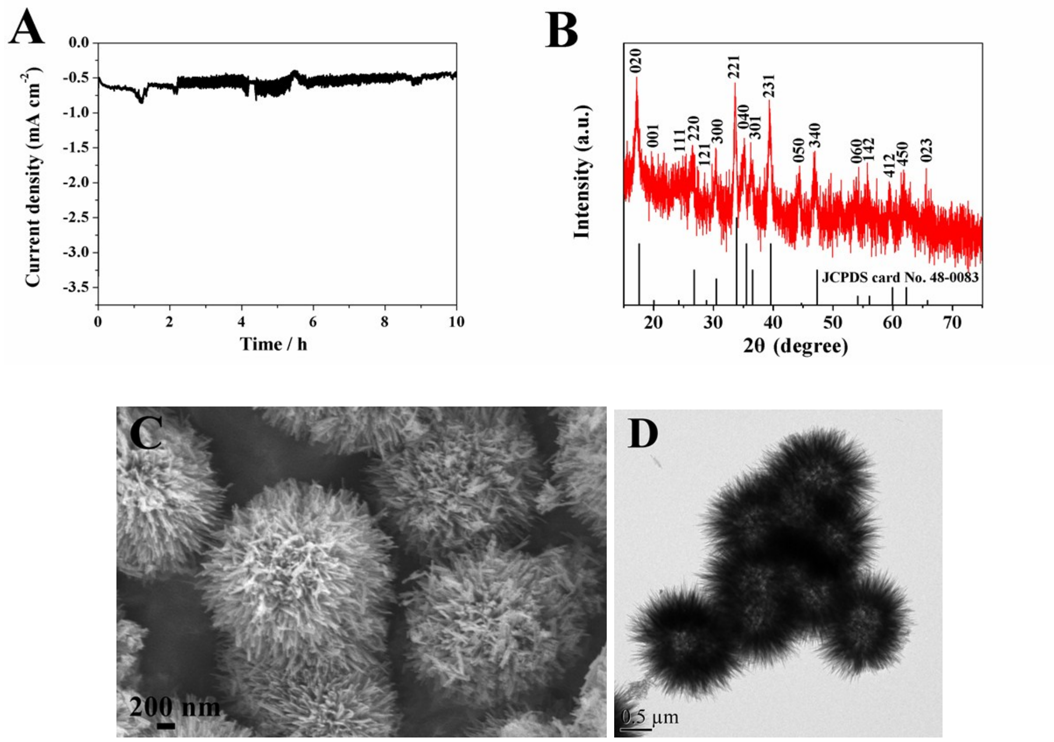

Fig. S10 (A) Constant-potential electrolysis at −0.98 V (vs. SCE) for 10 h in 0.1 M $NaHCO_3$ aqueous solution with CO_2 flow at the hollow urchin-like $Co(CO_3)_{0.5}(OH)\cdot 0.11H_2O$. (B) XRD pattern, (C) SEM image and (D) TEM image of hollow urchin-like $Co(CO_3)_{0.5}(OH)\cdot 0.11H_2O$ electrocatalyst after 10 h electrolysis.

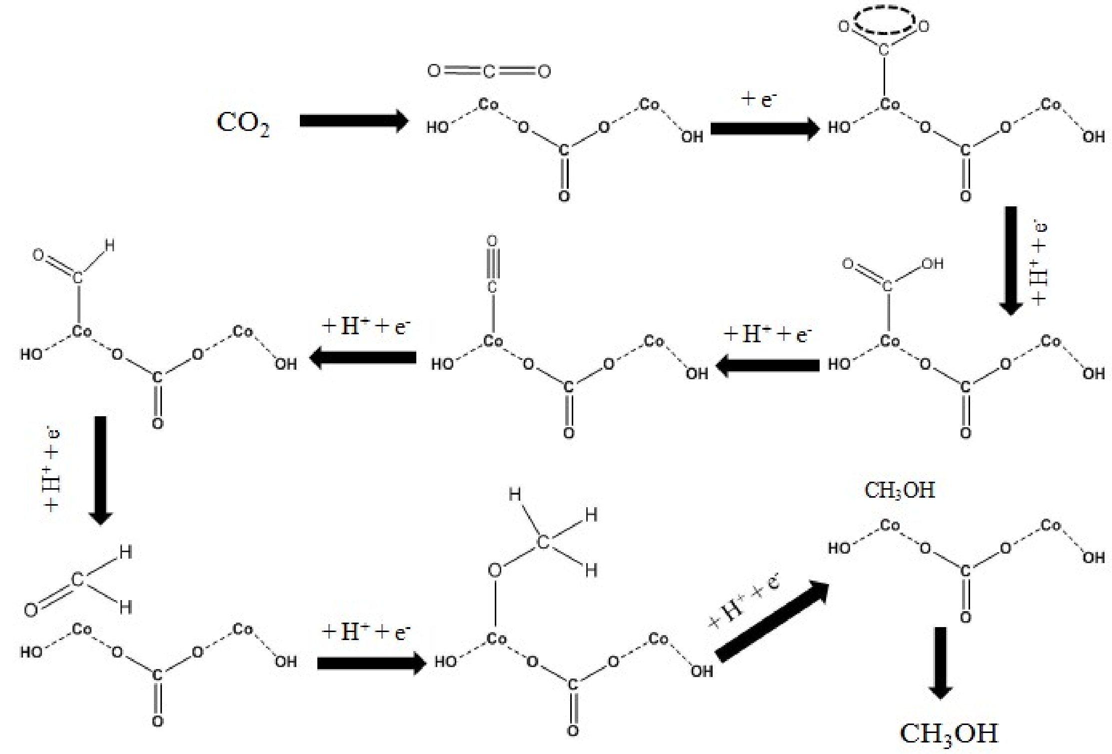

Fig. S11 Possible high selectivity reaction mechanism for electrochemical reduction of CO_2 to CH_3OH on hollow urchin-like $Co(CO_3)_{0.5}(OH)\cdot 0.11H_2O$ electrocatalyst in aqueous solution.

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