Supporting information

Relationships between surface hydrophilicity of a bismuth electrode and product selectivity of electrocatalytic CO_2 reduction

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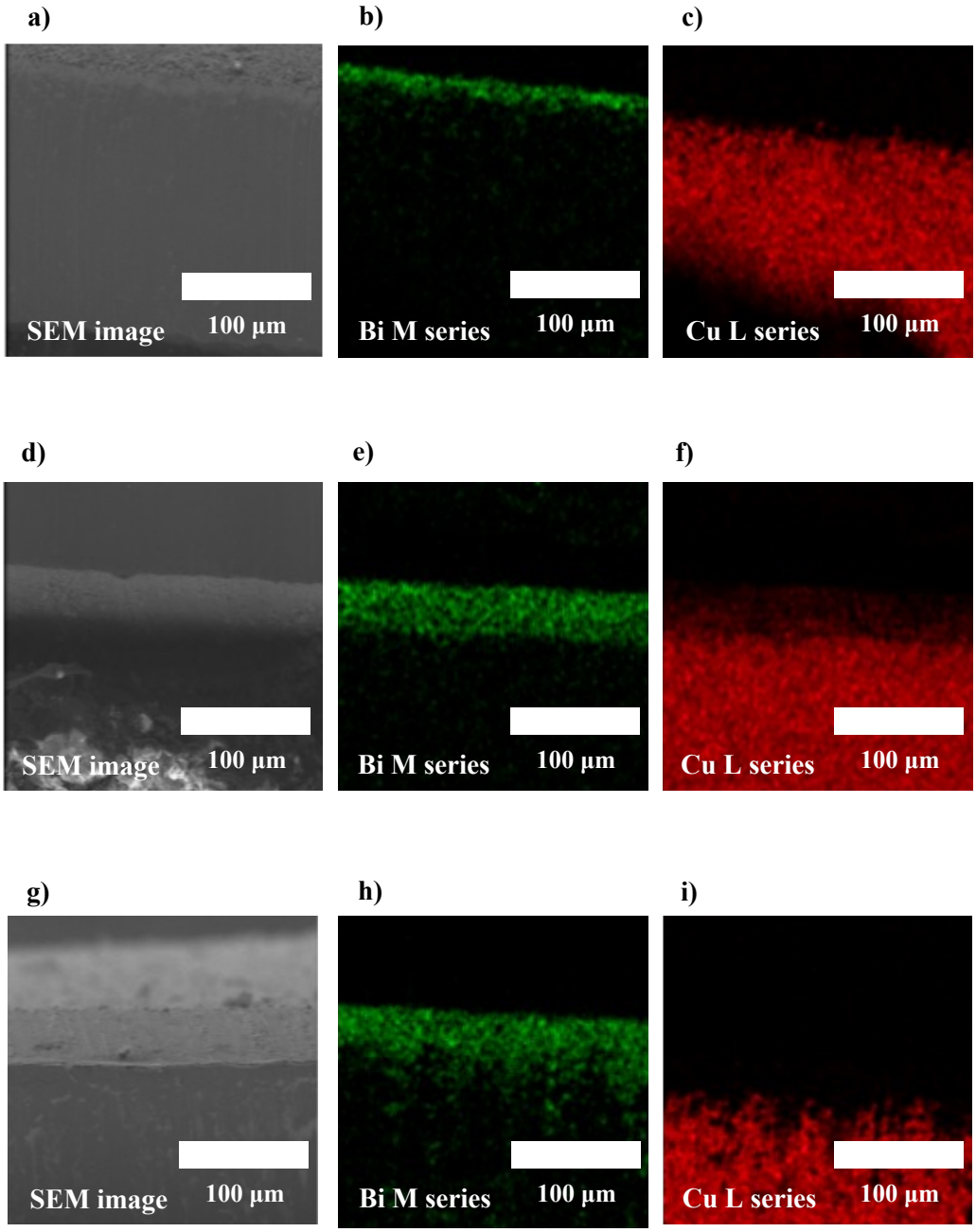


Figure S1. The results of EDS-mapping analysis on cross-sectional SEM images of three nano-Bi samples (top: micro-Bi-180s, middle: micro-Bi-300s, and bottom: micro-Bi-1800s). a) The cross-sectional SEM image, EDS mapping images of b) Bi M series, and c) Cu L series of micro-Bi-180s. d) The cross-sectional SEM image, EDS mapping images of e) Bi M series, and f) Cu L series of micro-Bi-300s. g) The cross-sectional SEM image, EDS mapping images of h) Bi M series, and i) Cu L series of micro-Bi-1800s.

Details on the determination of X-ray penetration depth of XRD analysis.

X-ray penetration depth was calculated using following equation,

$$\frac{I}{I_o} = e^{(-\mu/\rho)\rho}$$

where I and I_o are the intensity of X-ray out of the sample surface and coming into the sample surface, respectively. - μ/ρ is the mass attenuation coefficient of an element consisinting the sample and ρ is the density of the sample.

We assume the X-ray detection limit of 1 % of X-ray irradiating into the sample, then the analyzing depth of XRD analysis can be calculated using following equation,

$$d(cm) = \frac{4.36}{(-\mu/\rho)\rho}$$

The attenuation coefficient and nominal density of bismuth films for Cu K-alpha radiation (8.04 keV) was found in NIST.gov (National Institute of Standards and Technology) (2.2756×10^2 and 9.73 g/cm^3)

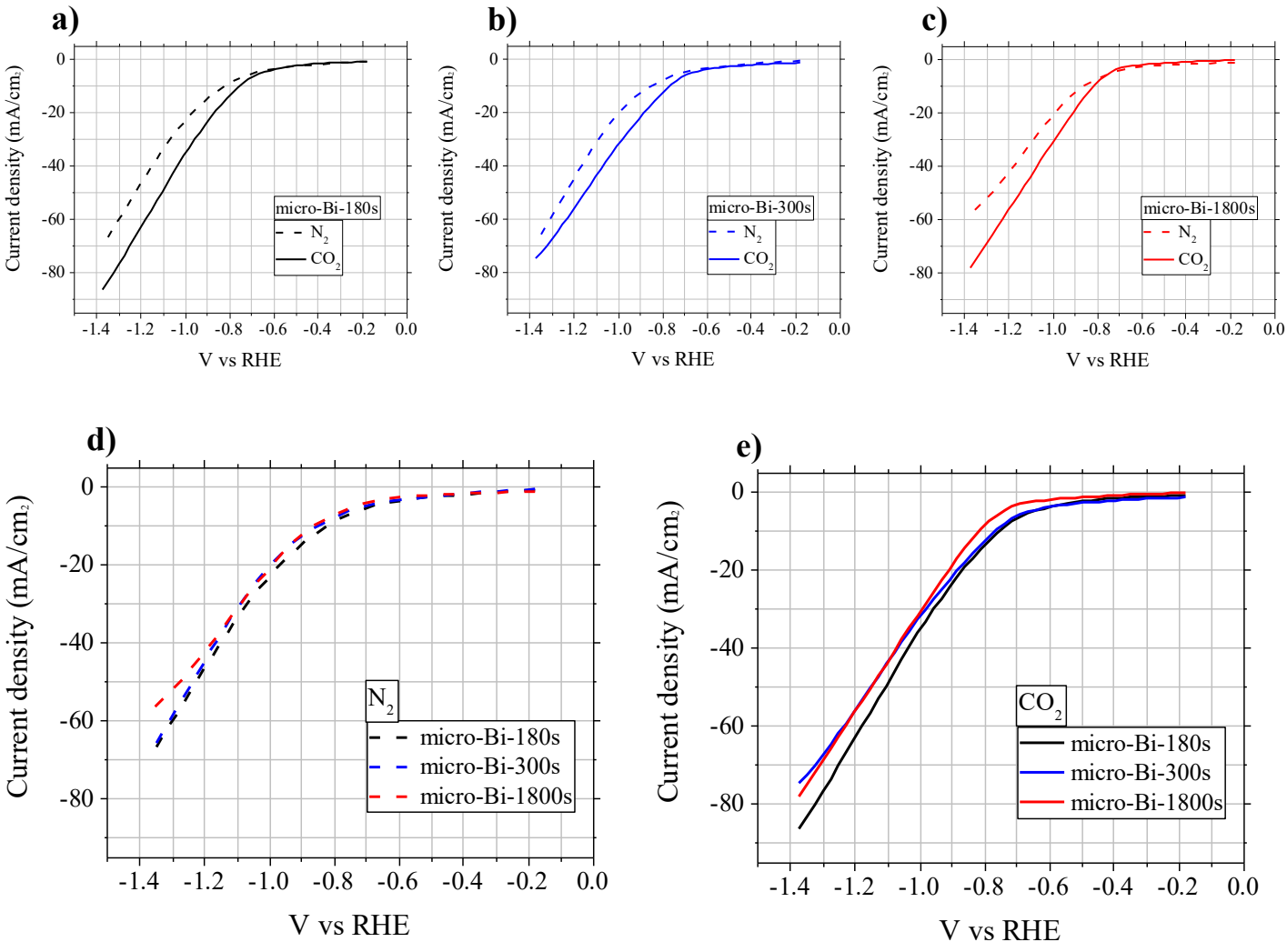


Figure S2. The results of LSV measurements with a) micro-Bi-180s, b) micro-Bi-300s, and c) micro-Bi-1800s under N_2 and CO_2 flow. Comparisons of LSV curves of micro-Bi-180s, micro-Bi-300s, and micro-Bi-1800s d) under N_2 and e) CO_2 flow.

Detailed information on the FE% calculation

Faraday efficiency (FE%) for formate was calculated as follows,

$$\text{F}ormate\ FE\% = \frac{n_{formate} \times 2 \times F}{\int_0^t I\ dt}$$

where $n_{formate}$ is the number of produced formate molecules by electrocatalytic CO_2 reduction, which was determined from NMR signal intensity using the calibration curve predetermined with standard formate solutions. The number of produced formate was multiplied by 2, the number of electrons required to form a formate. F is the Faraday constant (96485.3321 C/mol), and denominators of the above equation is the integrated current over the reaction time.

FE% for gaseous products (CH_4, CO, and H_2) were calculated as follows,

$$CH_4\ FE\% = \frac{n_{CH_4} \times 8 \times F}{I}$$

$$CO\ FE\% = \frac{n_{CO} \times 2 \times F}{I}$$

$$H_2\ FE\% = \frac{n_{H_2} \times 2 \times F}{I}$$

$n_{CH_4}, n_{CO}, n_{H_2}$ are the number of produced molecules per one second which were determined as follows,

$$n = vol\% \times \frac{1}{100} \times \frac{0.02\ L}{min} \times \frac{1\ min}{60\ s} \times \frac{1\ mol}{22.4\ L}$$

vol% is the volume concentration of each product molecule obtained from GC peak area using the respective calibration curve. It was multiplied by mass flow rate of the reactant gas (20 ml/min) and time unit is converted into seconds by multiplying parity relation between minute and second (1 min/60s). Then, volume of each product molecule is converted into the number of molecules in moles assuming its' perfect gas behavior at STP (22.4L/mol).

The number of produced molecules per one second was multiplied by the number of electrons required to form a particular product molecule. The numbers of electrons required for production of one CH_4, CO, and H_2 are 8, 2, and 2, respectively. F is the Faraday constant (96485.3321 C/mol), and denominators of the above equations are the currents measured during the CO_2 reduction (C/second).

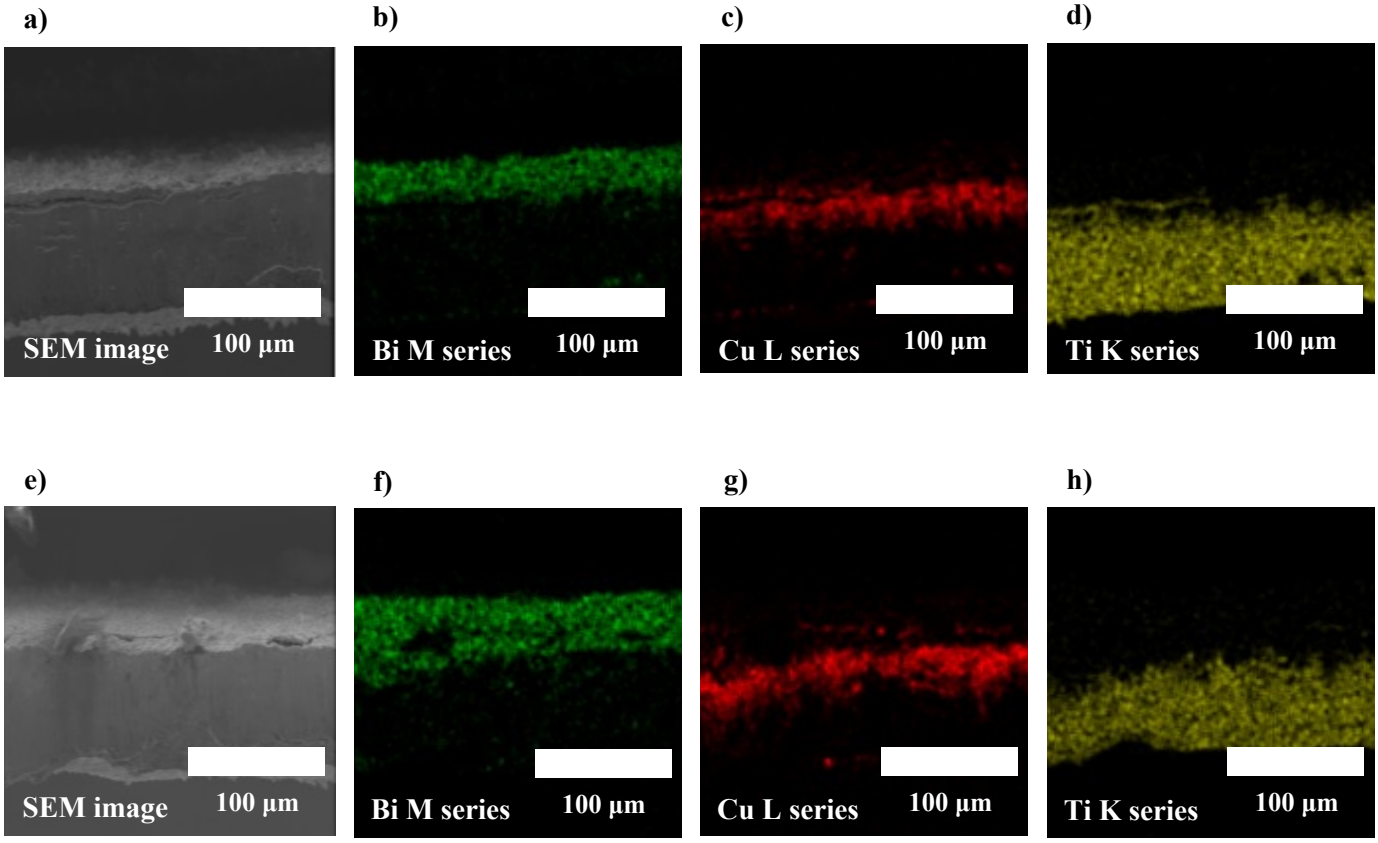


Figure S3. The results of EDS-mapping analysis on cross-sectional SEM images of two nano-Bi samples (top: nano-Bi-180s and bottom: nano-Bi-300s). a) The cross-sectional SEM image, EDS mapping images of b) Bi M series, c) Cu L series, and d) Ti K series of nano-Bi-180s. e) The cross-sectional SEM image, EDS mapping images of f) Bi M series, g) Cu L series, and h) Ti K series of nano-Bi-300s.

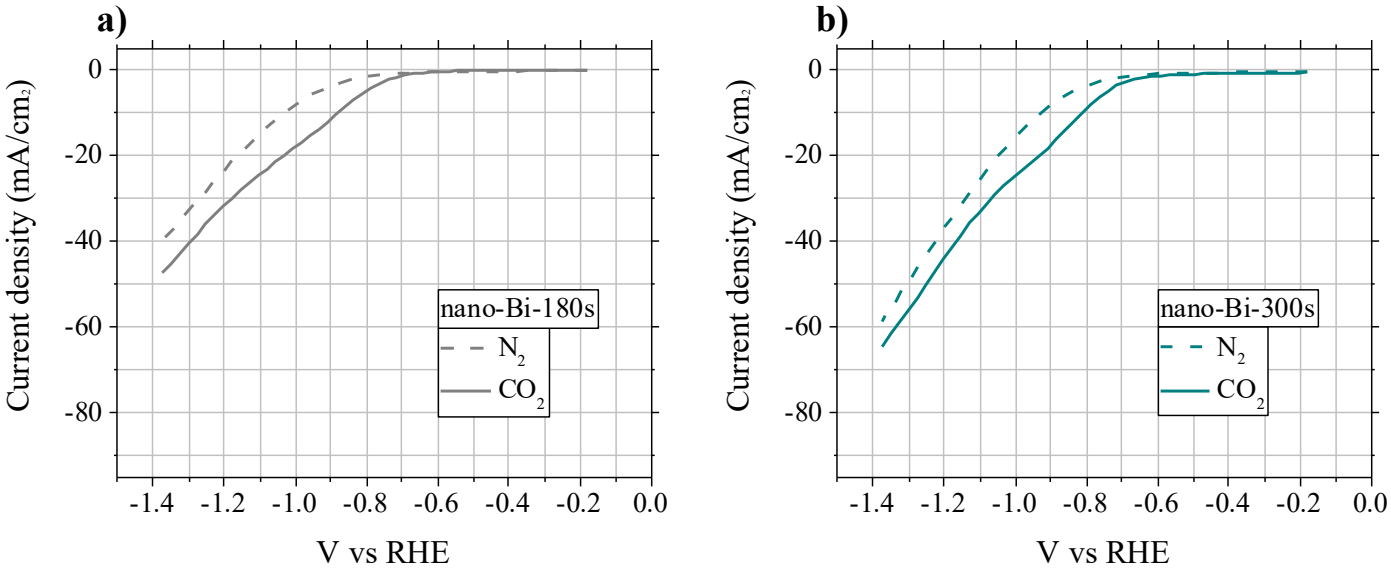


Figure S4. The results of LSV measurements with a) nano-Bi-180s and b) nano-Bi-300s under N_2 and CO_2 flow.

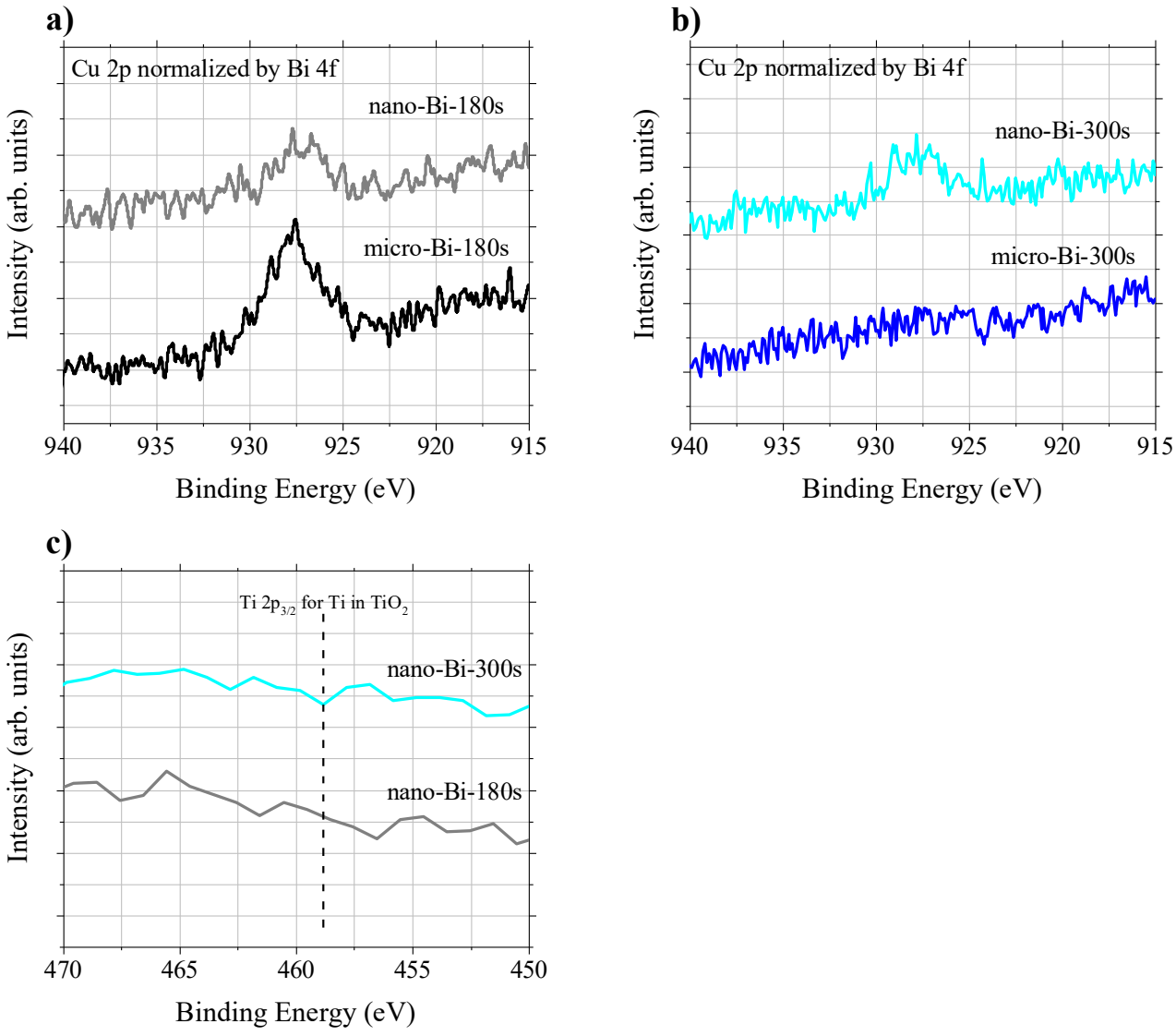


Figure S5. Cu 2p core-level XPS spectra of a) micro-Bi-180s and nano-Bi-180s, b) micro-Bi-300s and nano-Bi-300 after intensity normalization with respect to the respective Bi 4f core-level XPS spectra. c) Ti $2p_{3/2}$ core-level XPS spectra of nano-Bi samples.

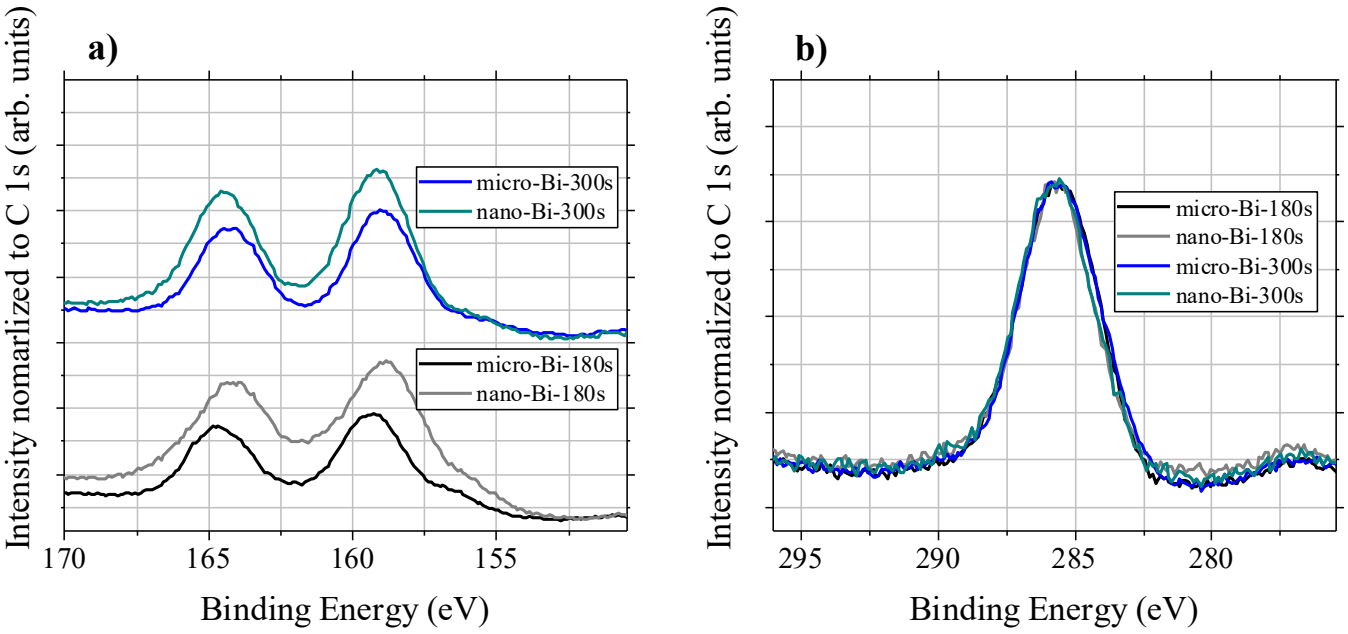


Figure S6. a) Bi 4f and b) C 1s core-level XPS spectra of four samples (micro-Bi-180s, nano-Bi-180s, micro-Bi-300s, and nano-Bi-300) after intensity normalization with respect to the respective C 1s core-level XPS spectra.

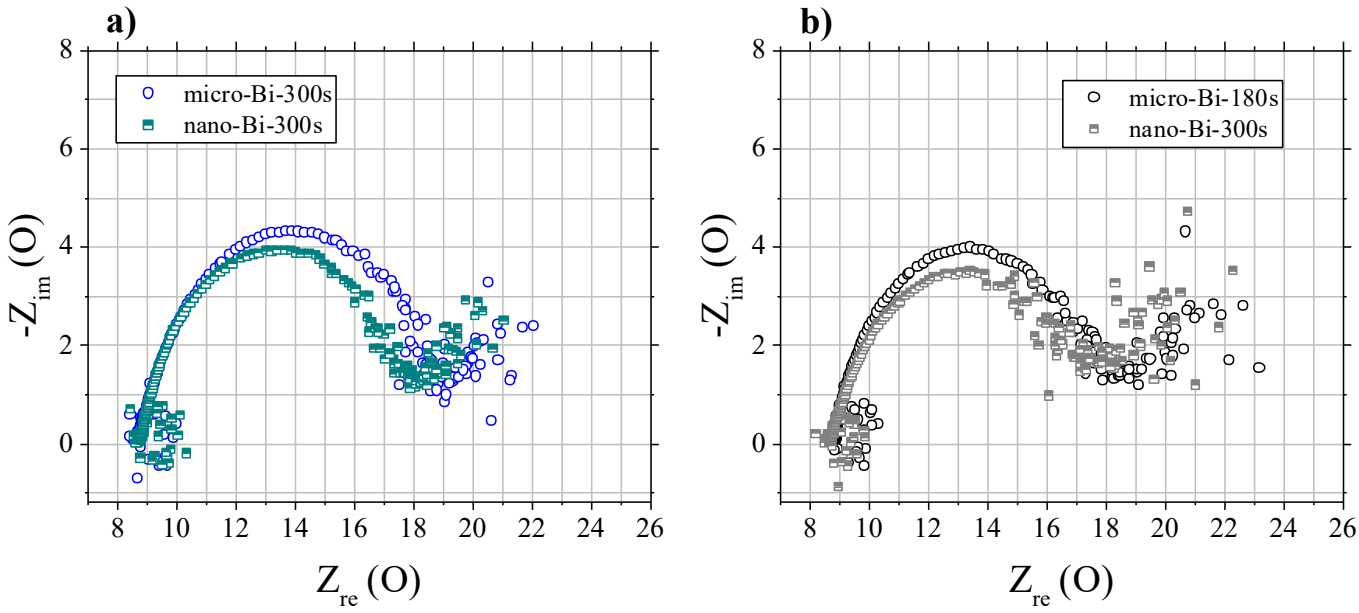


Figure S7. The Nyquist plots from EIS analysis of a) micro-Bi-180s and nano-Bi-180s, and b) micro-Bi-180s and nano-Bi300s.

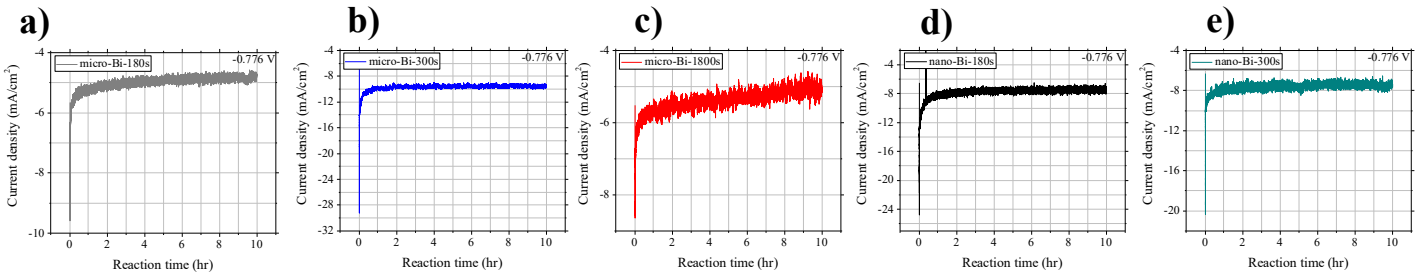


Figure S8. Current density as a function of reaction time (10 hrs) at -0.776 V of a) micro-Bi-180s, b) micro-Bi-300s, c) micro-Bi-1800s, d) nano-Bi-180s, and e) nano-Bi-300s.

	Formate FE% (-0.776 V)	
	Short-term (30 min)	Long-term (10 hrs)
micro-Bi-180s	93.55	92.73
micro-Bi-300s	93.38	90.03
micro-Bi-1800s	84.07	83.96
nano-Bi-180s	84.99	84.84
nano-Bi-300s	89.72	81.46

Table S1. Formate FE% for short-term and long-term CO2RR (-0.776 V).

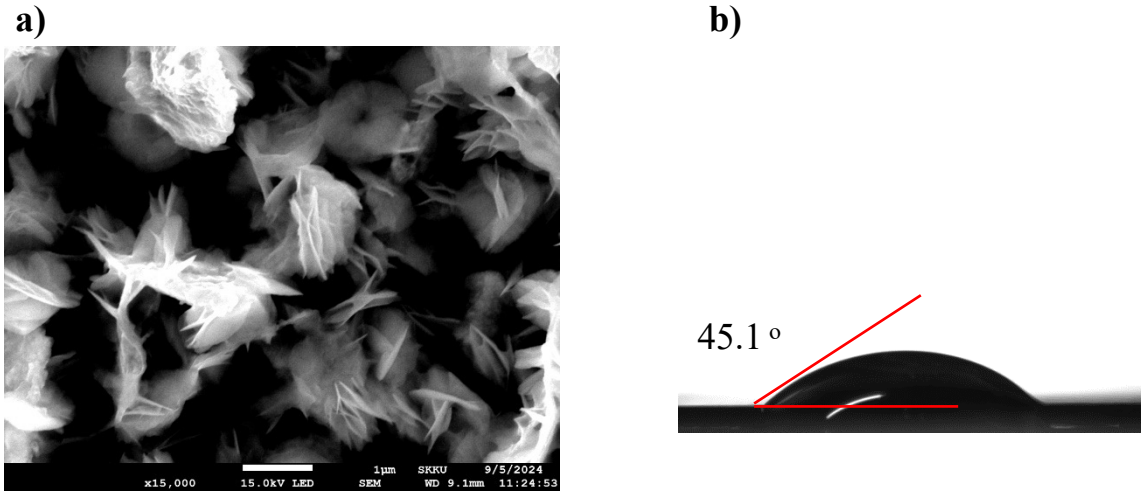
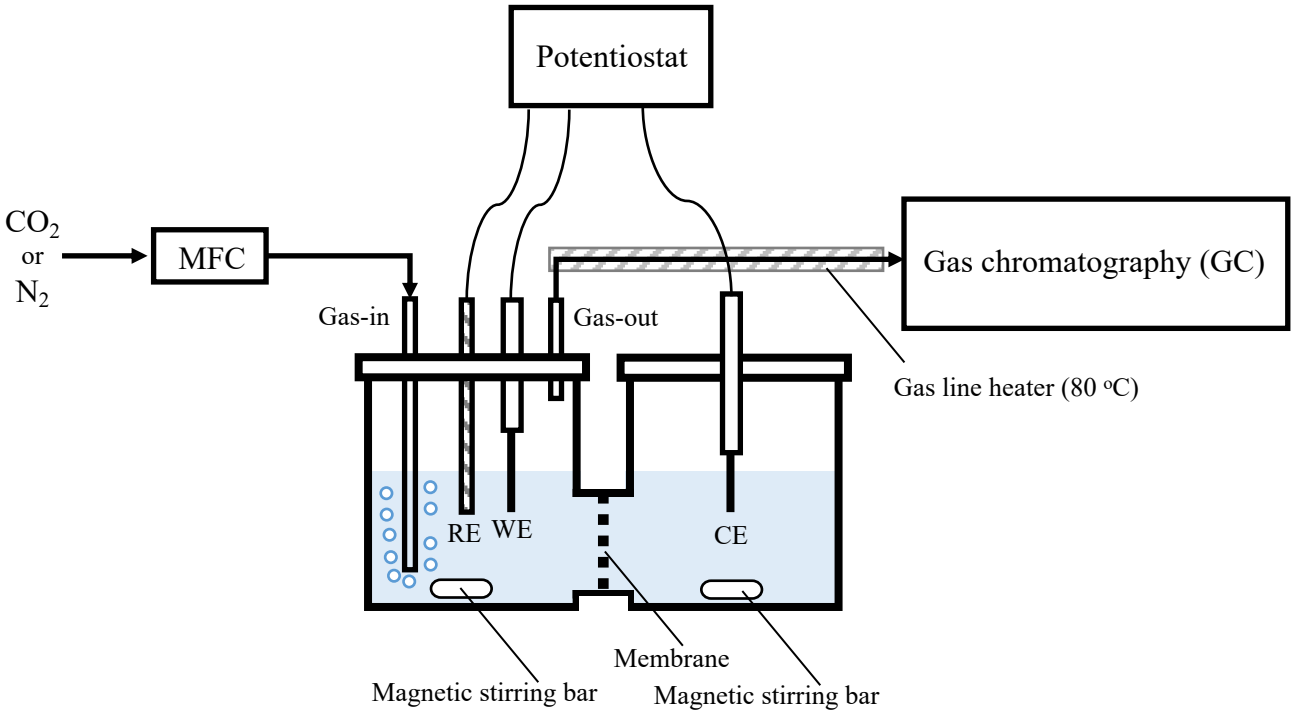


Figure S9. a) Topological SEM image of micro-Bi-300s after 10 hrs of CO2RR at -0.776 V, and b) the result of water contact angle measurement of micro-Bi-300s after 10hrs of CO2RR at -0.776 V.



Scheme S1. Schematic of experimental set-up for electrocatalytic CO_2 reduction.