

# Supporting Information

## Boosting Small-Molecule Reduction with Bismuth-Based Nanostructured Reactors

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## Electrochemical measurements

**Electrochemical NtrRR.** For NtrRR tests, potentiostatic tests were carried out in 0.05M KNO<sub>3</sub> without feeding CO<sub>2</sub> (under Ar gas) in a three-electrode H-cell. The volume of the electrolyte in the anode and cathode chamber is 45ml for each.

**Electrochemical CO<sub>2</sub>RR.** The CO<sub>2</sub>RR performances were evaluated in a three-electrode H-cell with CO<sub>2</sub>-saturated 0.1M KHCO<sub>3</sub>.

**Electrochemical coRR.** The coRR performances were evaluated in a three-electrode H-cell with CO<sub>2</sub>-saturated 0.1M KHCO<sub>3</sub> and 0.05M KNO<sub>3</sub>.

## Material synthesis

**The synthesis of Mixed Bi/C.** The main difference of synthesis routine between Mixed Bi/C and NR-Bi@C is that the metal ion loading time is shortened from 12 hours to 2 hours, so that the metal ions remain only near the surface of the nano-colloidal spheres, and after heat treatment, the nanoparticles can form on the surface of the carbon spheres.

The detailed steps for the preparation of hollow nanospheres are as follows: Initially, 510 mg of 2,4-dihydroxybenzoic acid (DA) and 192 mg of hexamethylenetetramine (HMT, urotropine) were dissolved in 144 ml of aqueous solution and stirred uniformly to form solution A. Then, 201 mg of sodium oleate (SA) was dissolved and heated in 48 ml of water, and 119.6 mg of P123 was dissolved and heated in 48 ml of water. Subsequently, P123 and SA were mixed at a 1:1 ratio and stirred to obtain solution B. The above solutions were mixed and placed in a polytetrafluoroethylene autoclave at 160 °C for 2 h. After the reaction, the product was centrifuged and washed with water three times to obtain hollow nanospheres. Metal salts loading: A metal salts with a mass ratio of 20% relative to the hollow carbon spheres was added and dissolved in water at 50 °C. The mixed solution was ultrasonicated for 30 min. After sonication, the solution was placed at 50 °C for metal ions adsorption for **2 h**. After the adsorption process, the solution was centrifuged twice and dried at 50 °C. The obtained powder was annealed in a tube furnace at 500 °C under H<sub>2</sub> atmosphere for 2 h to obtain Mixed Bi/C.

## Products determination

**Determination of gaseous products.** The gaseous products (CO and H<sub>2</sub>) for CO<sub>2</sub>RR and co-reduction were quantified on a GC-2014 (Shimadzu) gas chromatograph connected to the headspace of the electrolysis cell. A thermal conductivity detector (TCD) was used to quantify H<sub>2</sub>, and a flame ionization detector (FID) equipped with a methane reformer was used to quantify CO, CH<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>6</sub>.

**Determination of formate.** The formate is quantified by 500M HZ NMR

**Determination of ammonia.** Ammonia is determined by *indophenol blue method*. First, a 2ml aliquot of the solution was removed from the electrochemical reaction vessel. Then 2ml of a 1M NaOH solution containing 5wt% salicylic acid and 5wt% sodium citrate was added, followed by addition of 1ml of 0.05M NaClO and 0.2ml of an aqueous solution of 1wt% sodium nitroferricyanide. After 2h at room temperature, the absorption spectrum was measured using a UV–Vis spectrophotometer (Shimadzu UV-2700). The formation of indophenol blue was determined using the absorbance at a wavelength of 655nm. The concentration–absorbance curves were calibrated using standard ammonia sulfate solutions, as shown in Fig. S7, which contained the same concentrations of electrolytes as used in the electrocatalysis experiments.

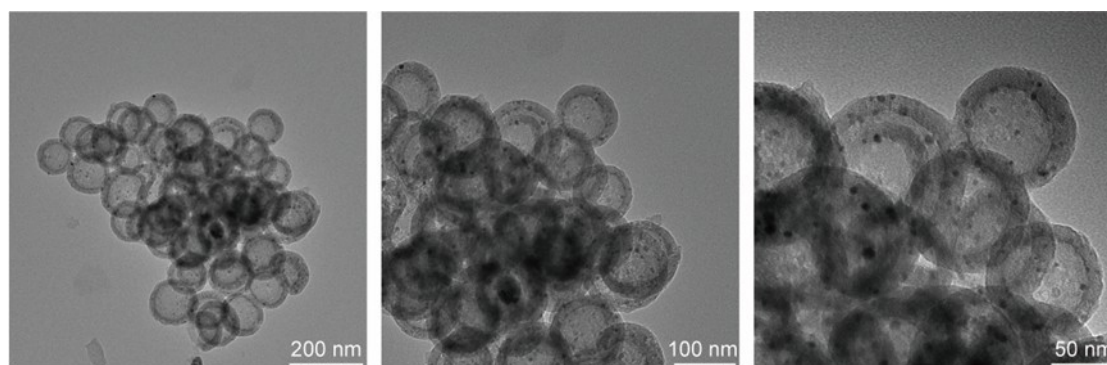
**Determination of NO<sub>2</sub><sup>-</sup>.** Nitrite was determined after diluting electrolyte by colorimetry based on the Griess reaction. Two reagents were prepared and stored at 4 °C, including a) solution A, containing 10 mg mL<sup>-1</sup> of sulfanilamide and 1.2 M HCl; and b) solution B, containing 1.0 mg mL<sup>-1</sup> of *N*-(1-Naphthyl)ethylenediamine dihydrochloride (NED). Specifically, the coloring reagent was prepared by mixing equal volumes of solutions A and B. 0.6 mL of the coloring reagent was then mixed with 4 mL of the neutralized sample solution at room temperature. The absorbance measurement was performed on a UV-Vis spectrophotometer (Shimadzu UV-2700) at a wavelength of 540 nm after 15 min of color development. T

**Determination of urea.** Urea is determined by *diacetyl monoxime method*. *Diacetyl monoxime method*. Initially, a 1 mL aliquot of the reaction solution was extracted from the electrochemical cell. Subsequently, 2 mL of acid-ferric reagent (prepared by mixing 100 mL concentrated phosphoric acid, 300 mL concentrated sulfuric acid, 600 mL

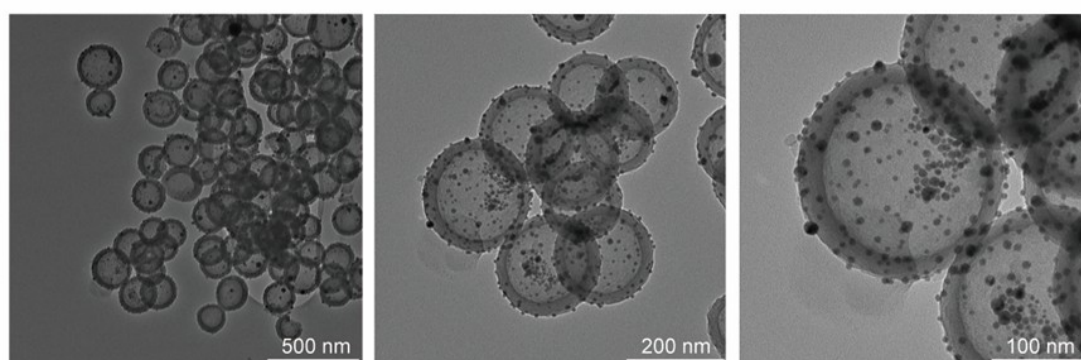
deionized water, and 100 mg ferric chloride) and 1 mL of diacetylmonoxime-thiosemicarbazide (DAMO-TSC) reagent (a solution containing 5 g DAMO and 100 mg TSC dissolved in 1000 mL deionized water) were introduced. The mixture was then subjected to heating at 100°C for 20 minutes. Following cooling to ambient temperature, the absorbance was measured at 525 nm utilizing a UV-Vis spectrophotometer (Shimadzu UV-2700).

**Finite element simulation.** COMSOL Multiphysics software was used to simulate the influence on mass transfer and species concentration distribution. Tertiary Current Distribution module coupled with Transport of Diluted Species was used to calculate the concentration distribution. The reactant concentration was set as 10 mM based on experiments.

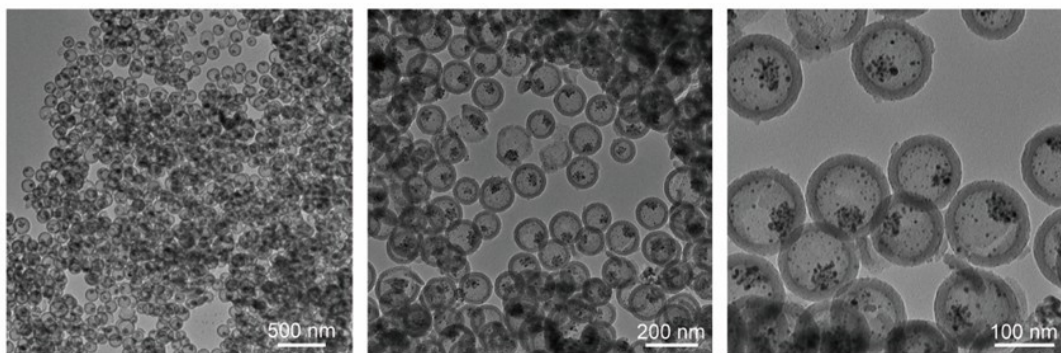
## Figures



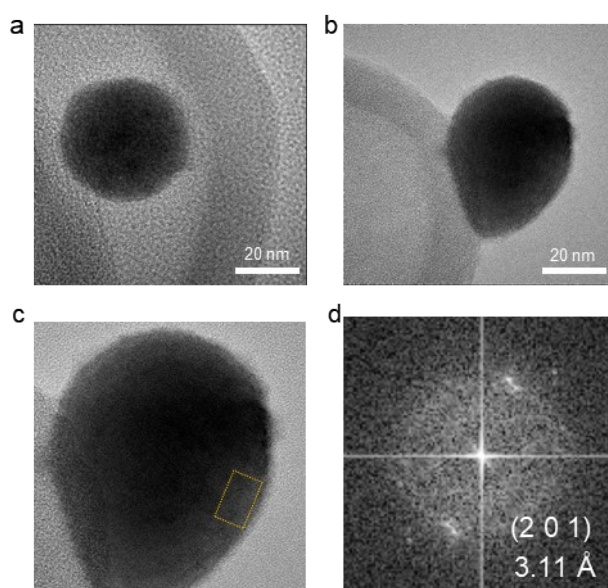
**Fig. S1.** The TEM images of synthesized NR-Sn@C.



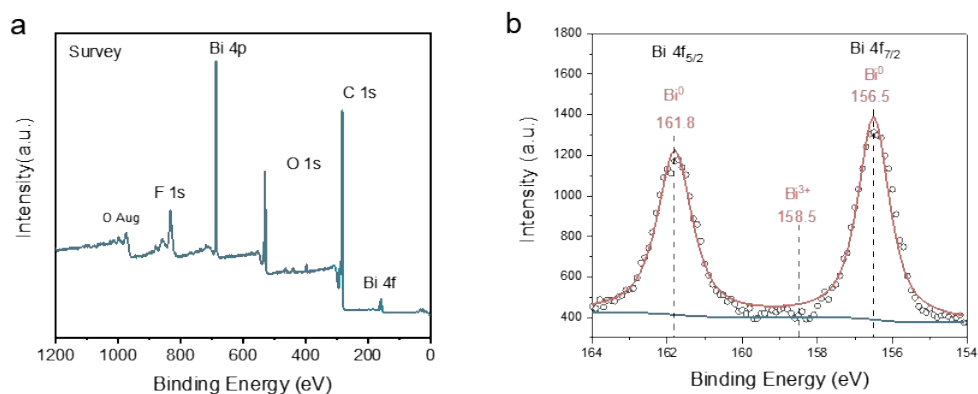
**Fig. S2.** The TEM images of synthesized NR-In@C.



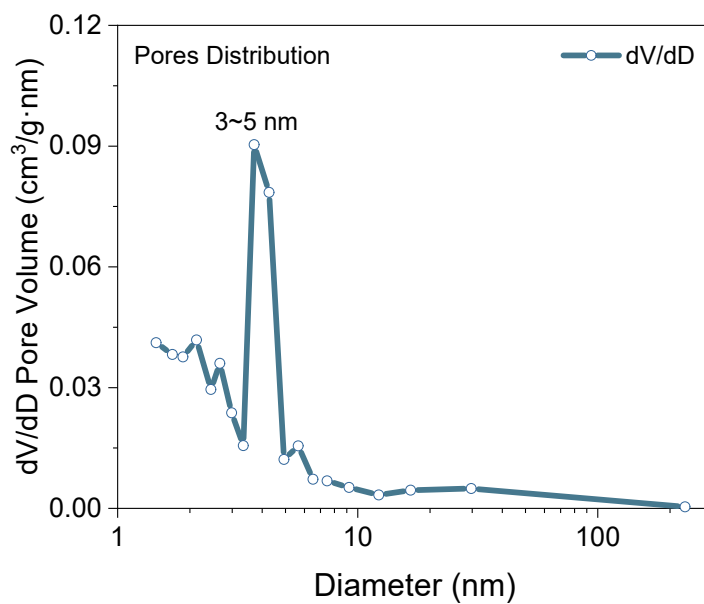
**Fig. S3.** The TEM images of synthesized NR-Pd@C.



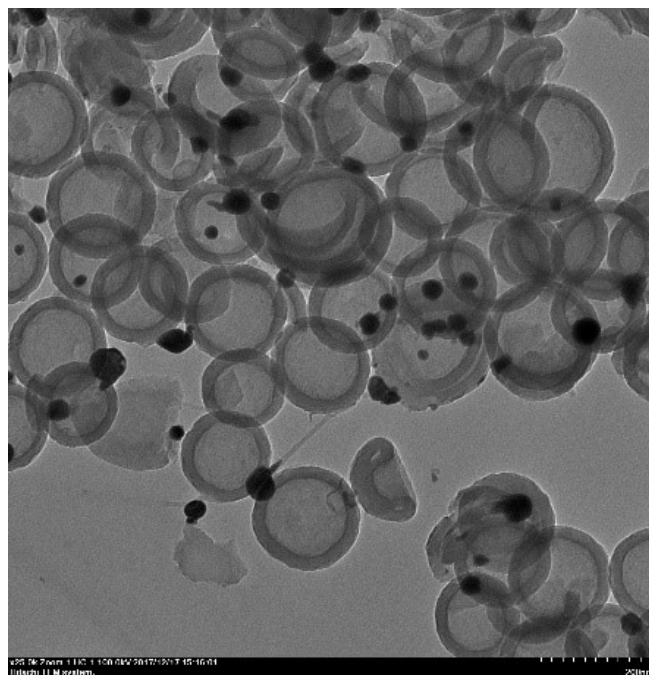
**Fig. S4.** (a) The HRTEM of NR-Bi@C and (b) Mixed Bi/C respectively. (c) HRTEM image of Bi nanoparticle and (d) corresponding selected area electron diffraction.



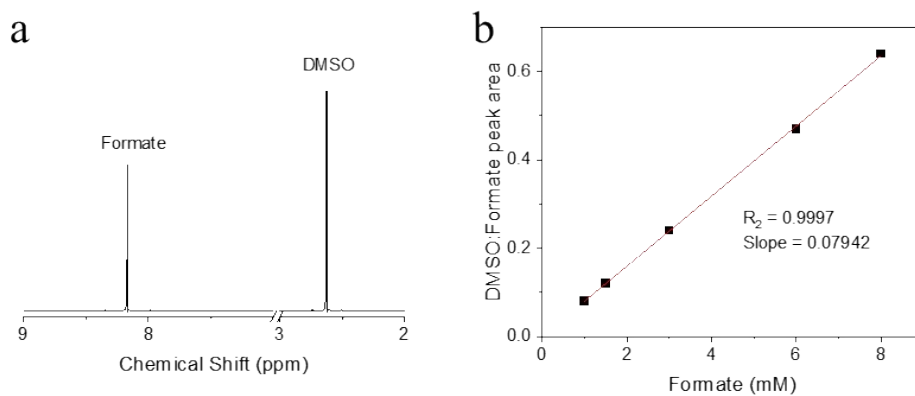
**Fig. S5.** The XPS spectra of synthesized NR-Bi@C.



**Fig. S6.** Mesopores (2 ~ 50 nm) and macropores (>50 nm) distribution of NR-Bi@C.

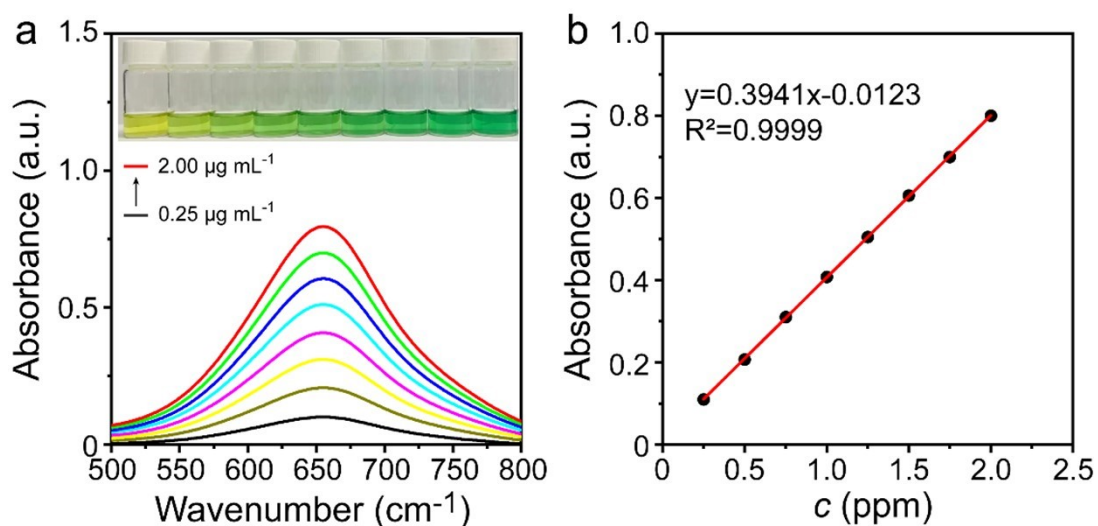


**Fig. S7.** The TEM images of Mixed Bi/C in which Bi nanoparticles are outside of hollow nanosphere.

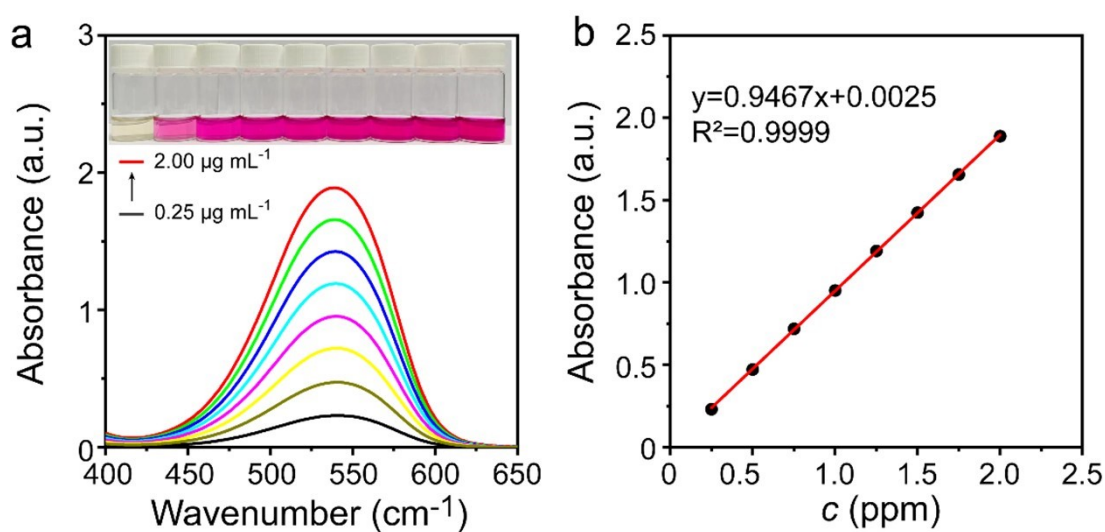


**Fig. S8.** (a)  $\text{H}^1$  NMR spectrum of cathodic electrolyte after  $\text{CO}_2\text{RR}$ . (b) The plot of concentration with the peak-area ratio for formate/DMSO.

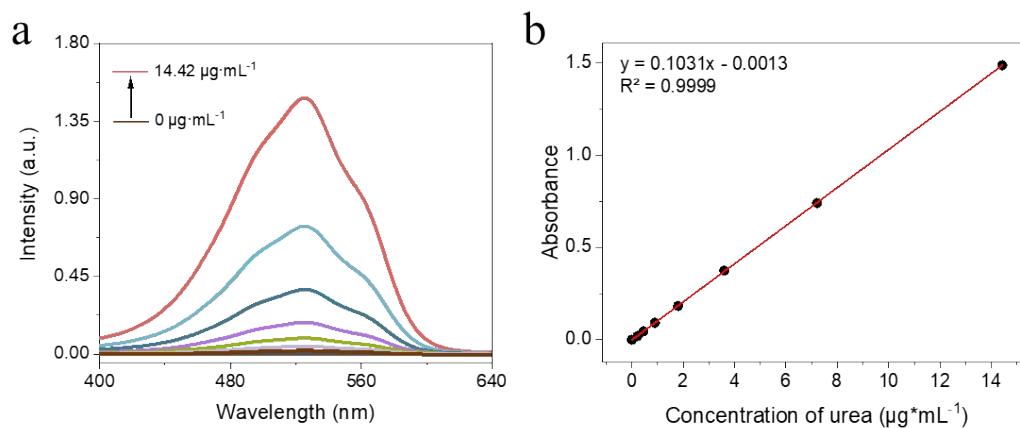




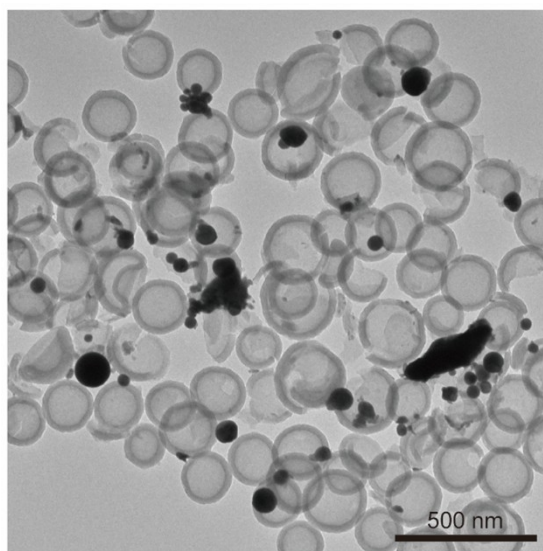
**Fig. S9.** Standard curves of prepared of ammonium chloride without urease. (a) UV-Vis curves measured by indophenol blue color development. (b) Linear relationship between ammonium chloride concentration and absorbance at 655 nm (The base of solvent contains 0.1 M  $\text{KHCO}_3$  and 0.05 M  $\text{KNO}_3$ ).



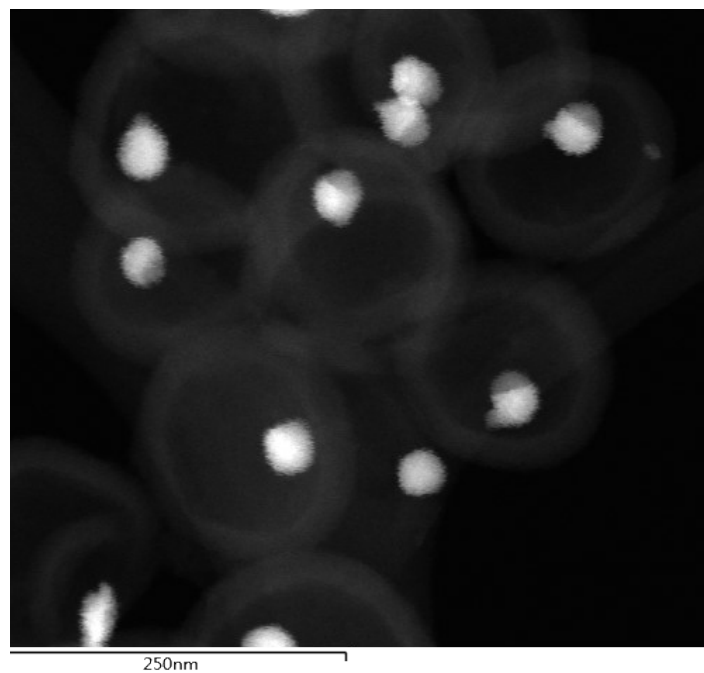
**Fig. S10.** Standard curves of prepared  $\text{KNO}_2$  solution. (a) UV-Vis curves. (b) Linear relationship between nitrite concentration and absorbance at 540 nm (The base of solvent contains 0.1 M  $\text{KHCO}_3$  and 0.05 M  $\text{KNO}_3$ ).



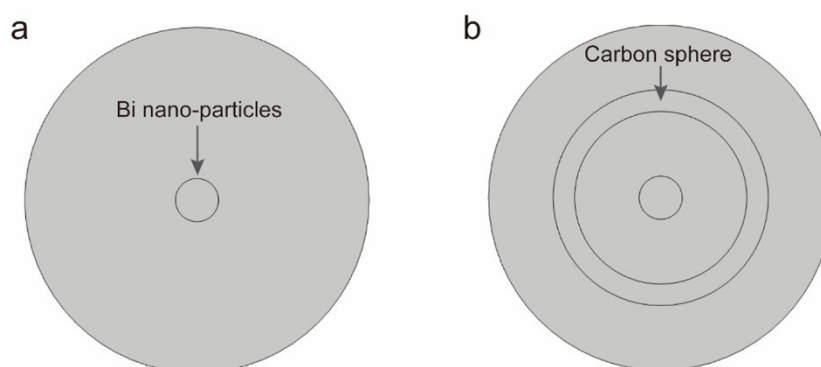
**Fig. S11.** Standard curves of urea solution. (a) UV-Vis curves measured by *diacetyl monoxime method*. (b) Linear relationship between urea concentration and absorbance at 540 nm.



**Fig. S12.** The TEM of Mixed Bi/C after 100 hours coRR.



**Fig. S13.** The TEM images of NR-Bi@C after 100 hours coRR.



**Fig. S14.** The original model diagrams for COMSOL (without contact with the electrolyte).

## Tables

**Table S1.** The elements analysis by ICP-OES for NR-Bi@C and Mixed Bi/C.

|            | Bismuth (wt %) |
|------------|----------------|
| NR-Bi@C    | 37.6           |
| Mixed Bi/C | 30.8           |

**Table S2.** The optimal Faraday efficiency for urea, formate and ammonia productions of some recently reported Bi-based catalysts.

| Catalysts                                         | Optimal<br>FE @ ( V vs.RHE)                                                                                       | References                                                |
|---------------------------------------------------|-------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------|
| NR-Bi@C                                           | FE <sub>urea</sub> =16.93% (@-0.70 V)<br>FE <sub>HCOOH</sub> =85% (@-0.80 V)<br>FE <sub>NH3</sub> =80% (@-0.60 V) | <i>This work</i>                                          |
| GB-rich Bi                                        | FE <sub>urea</sub> =32% (@-0.40 V)                                                                                | <i>Angew. Chem. Int. Ed.</i> <b>2024</b> , 63, e202318589 |
| O-BiM/CuOX                                        | FE <sub>urea</sub> =23.5% (@-0.60 V)                                                                              | <i>J. Am. Chem. Soc.</i> <b>2024</b> , 146, 25813–25823   |
| $\alpha$ -SnBi NS/rGO                             | FE <sub>urea</sub> =78.36% (@-0.40 V)                                                                             | <i>J. Am. Chem. Soc.</i> <b>2024</b> , 146, 13527–13535   |
| Bimetallic Cu-Bi                                  | FE <sub>HCOOH</sub> =92% (@-1.0 V)                                                                                | <i>Angew. Chem. Int. Ed.</i> <b>2023</b> , 62, e202217569 |
| Bi <sub>1</sub> -HOF                              | FE <sub>HCOOH</sub> =90% (@-1.0 V)                                                                                | <i>Angew. Chem. Int. Ed.</i> <b>2024</b> , 63, e202404015 |
| BiOBr                                             | FE <sub>HCOOH</sub> =91% (@-1.05 V)                                                                               | <i>Nat. Catal.</i> <b>2023</b> , 6, 796–806               |
| Bi@C nanosheets                                   | FE <sub>NH3</sub> =15.10% (@-0.4V)                                                                                | <i>Adv. Funct. Mater.</i> <b>2021</b> , 31, 2100300       |
| Bi-N-C                                            | FE <sub>NH3</sub> =88.7% (@-0.35V)                                                                                | <i>Adv. Sci.</i> <b>2023</b> , 10, 2302623                |
| Bi <sub>1</sub> -CuCo <sub>2</sub> O <sub>4</sub> | FE <sub>NH3</sub> =95.53% (@-0.80V)                                                                               | <i>Adv. Funct. Mater.</i> <b>2024</b> , 34, 2409696       |