

Nanoreactor Based on Cyclodextrin for Direct Electrocatalyzed Ammonia Synthesis

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Cite This: ACS Nano 2022, 16, 18398-18407 **Read Online** ACCESS Article Recommendations Metrics & More s Supporting Information ABSTRACT: The high-efficiency transition metal-free electro- \mathbf{v} (1) (2)catalytic nitrate reduction reaction (NO₃⁻RR) for ammonia ee synthesis has received more attention because of its green and environmentally friendly characteristics. Here, we report an efficient electrochemical NH₃ synthesis directly from purely organic macrocyclic compounds α -, β -, and γ -cyclodextrins Faradaic efficiency Faradaic efficiency (CDs)-catalyzed transition metal-free electroreduction of NO 63.2% 79.3% NH₃ yield rate NH₃ yield rate: NH nitrate under ambient conditions. In comparison with α -, and 2.28 mg h⁻¹ cm⁻² 4.66 mg h⁻¹ cm⁻²

ance with a relatively higher NH₃ yield that can reach up to 2.28 mg h⁻¹ cm⁻² with a Faradaic efficiency (FE) of 63.2% at -0.9 V versus a reversible hydrogen electrode in alkaline medium, and the potassium ion-coordinated γ -CD complex can achieve a maximum NH₃ production rate up to 4.66 mg h⁻¹ cm⁻² with an NH₃ FE of 79.3%. Further comparison with permethyl- γ -CD, p-glucose, and poly(vinyl alcohol) for the NO₃⁻RR indicated that the typical torus-shaped cyclic conformation and edge hydroxyl groups of parent CDs play important roles in the electrocatalytic process. The K⁺-mediated 3D γ -CD-K⁺ frameworks containing six CDs as nanoreactors greatly strengthen the enrichment effect of nitrate through hydrogen-bonding interaction and electrostatic interaction and promote the mass transfer, thus leading to the efficient NO₃⁻RR in an alkaline electrolyte. This work provides a convenient, green, and economic method for high-performance NO₃⁻RR, which has potential applications in the fields of environment, energy, and industry.

Anode

Cathode

KEYWORDS: cyclodextrin, supramolecular chemistry, nanoreactor, ammonia synthesis, electrocatalysis, nitrate reduction reaction

INTRODUCTION

Ammonia (NH_3) synthesis has always been a challenging task due to its decisive role in industrial and agricultural production.¹⁻⁴ At present, the industrial production of NH₃ is still heavily dominated by the Haber Bosch process under the harsh conditions of high temperature and pressure, resulting in high energy consumption and greenhouse gas emission.⁵⁻⁸ Therefore, the exploration of a green and sustainable ammonia production process under clean and mild conditions is quite necessary. Electrocatalysis is one of the most intriguing highlights in the field of chemistry and energy materials because of its green and environmentally friendly characteristics, in which electrochemical reduction to synthesize NH₃ has attracted extensive attention such as an electrochemical nitrogen reduction reaction (ENRR), offering an alternative approach to NH₃ production.^{9,10} However, due to the high dissociation energy of the nitrogen-nitrogen triple bond (941 kJ mol⁻¹) and limited solubility of nitrogen in water, the ENRR suffers from the generally low reaction rate and Faraday efficiency (FE).^{11–13} When searching for a suitable nitrogen source to replace nitrogen for electrochemical ammonia synthesis, nitrate (NO3⁻) gradually emerged due to its relatively low bond dissociation energy (204 kJ mol⁻¹ for

 β -CDs, parent γ -CD presented uncommon catalytic perform-

nitrogen–oxygen), which also endowed the electrocatalytic process with better reaction kinetics and relatively decreased energy consumption.¹⁴ Moreover, the rapid accumulation of NO_3^- in the environment derived from the excessive usage of nitrogen-containing fertilizer and the discharge of industrial wastewater inevitably leads to NO_3^- -caused water pollution and poses a serious threat to human beings and the environment.^{15,16} Therefore, the electrocatalytic nitrate reduction reaction (NO_3^-RR) is an ideal option to transform this pervasive water pollutant into value-added NH₃, which simultaneously addresses the environmental problem.^{17,18}

Although NO_3^-RR catalysts based on noble metals (e.g., Au, Pd, Pt, Ru) exhibit benign catalytic activity, they are seriously plagued by high cost and scarcity, which impede their further wide application.¹⁹ Thus, electrocatalysts originating from transition metals (e.g., Fe, Ni, Cu, Mo) featuring comparatively

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low price and abundant reserve have drawn a great deal of interest.²⁰ For example, Wang and co-workers have reported a Fe single atom catalyst via a carbonization strategy showing efficient catalytic performance toward nitrate reduction to ammonia with a high NH₃ FE of about 75% and a yield rate that reached up to $0.46 \text{ mmol h}^{-1} \text{ cm}^{-2.21}$ Compared with the electrocatalysts described above, the metal-free catalysts have inherent advantages such as avoiding the release of metal ions and preventing secondary pollution to the environment.²²⁻²⁴ Metal-free catalysts such as boron carbide nanosheets and Ndoped porous carbon have been proved to be valid for ammonia synthesis via N₂ fixation,^{25,26} while similar catalysts applied in NO₃⁻RR are still rare and urgently needed. On the other hand, most electrocatalysts are obtained by hightemperature pyrolysis, which undoubtedly increases the difficulty of material preparation and energy consumption.² In addition, it is necessary to introduce a nitrogen source to realize metal anchoring coordination, which brings uncertainty to the origin of ammonia. Therefore, seeking cost-effective and environmentally friendly metal-free electrocatalysts to realize this process is still highly desirable and remains a great challenge.

Cyclodextrins (CDs) as cyclic oligosaccharides possessing a truncated cone conformation and well-defined molecular architecture have aroused enormous attention in material science and pharmaceutical chemistry.^{28,29} Moreover, CDbased catalysts could effectually facilitate asymmetric reactions with prominent enantioselectivity.^{30–33} In addition, it has been discovered that CDs can coordinate alkali metal ions to form a stable extended structure for sensing,^{34,35} gas absorption,³⁶⁻³⁸ separation,³⁹ and purification.⁴⁰ Recently, our group reported a cucurbit[8]uril-based two-dimensional supramolecular polypseudorotaxane for preparation of ultrafine Pt nanoparticles to realize electrochemical nitrogen fixation.⁴¹ However, the application of a supramolecular assembly based on purely organic macrocyclic compounds to electrochemical nitrate catalytic reduction has not been reported thus far to the best of our knowledge.

Herein, we report our recent finding that CD-based nanoreactors can achieve effective green metal-free NO3-RR with favorable FE and NH₃ yield under ambient conditions especially in an alkaline electrolyte. Parent α -, β -, and γ -CDs all exhibited definite electrocatalyzed performance, where γ -CD can achieve an NH₃ yield up to 2.28 mg h^{-1} cm⁻² with an NH₃ FE of 63.2% at -0.9 V versus a reversible hydrogen electrode (RHE). The electrocatalytic process was attributed to the distinctive torus-shaped cyclic structure of CDs, whose hydroxyl groups have affinity for anionic nitrate via a hydrogen-bonding interaction, thereby facilitating the electroreduction of nitrate over the electrode. Further experiments demonstrated that the cyclodextrin-potassium coordination $(\gamma$ -CD-K⁺) complex can achieve a maximum NH₃ production rate up to 4.66 mg h^{-1} cm⁻² with an NH₃ FE value of 79.3%, indicating that γ -CD-K⁺ complexes as nanoreactors achieved efficient enrichment of anionic nitrate through double functions (hydrogen-bonding interaction between hydroxyl groups and anionic nitrate; electrostatic interaction between complexed potassium ions and anionic nitrate) and accelerated mass transfer and thus enhanced the performance in NO₃-RR in an alkaline electrolyte (Scheme 1). ¹⁵N isotope-labeling experiments implied that the produced NH₃ was almost completely derived from nitrate reduction, and in situ FTIR measurement revealed a $NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow NH_3$

Scheme 1. Schematic diagram of the electrocatalytic NO_3^-RR for (1) γ -CD and (2) γ -CD-K⁺ complex in 0.1 M KOH/0.1 M KNO₃ electrolyte under ambient conditions.



pathway for NO₃⁻RR over γ -CD catalysts. This study not only offers an alternative approach for convenient and environmentally friendly electrochemical nitrate reduction reaction but also provides a green and economic method to design transition metal-free catalysts with high performance for the electrosynthesis of ammonia.

RESULTS AND DISCUSSION

 α -, β -, and γ -CDs are commercially available and directly used with literally no modifications. The framework γ -CD-K⁺ complex can be conveniently prepared via the vapor diffusion method using γ -CD and alkali metal cations according to the previous report.⁴² The FTIR spectra and corresponding XRD patterns of α -CD, β -CD, γ -CD, and the γ -CD-K⁺ complex are provided in Figures S1 and S2, confirming that the γ -CD-K⁺ complex was successfully prepared. First, we established a standard curve for the detection of NH₃ concentration via the indophenol blue method before the testing of electrocatalytic NO₃⁻RR performance. The NH₄Cl absorption standard curves were obtained in the range of 550–750 nm (Figure S3). Then, the concentration-absorbance standard curve of a NH₄Cl solution is established according to the standard solution absorbance at 656 nm. A standard three-electrode system was adopted to evaluate the electrocatalytic activity of nitrate reduction at atmospheric pressure and room temperature, where a 0.1 M KOH electrolyte with 0.1 M nitrate-N was placed in an H-type electrochemical cell separated by a Nafion membrane. The constant potential electrolysis method was used to test at different potentials for 1.0 h, respectively. After 1.0 h of electrolysis, the cathode electrolyte was collected, and the product NH₃ obtained in the electrocatalysis process was quantitatively analyzed by the indophenol blue method. Unless otherwise stated, the whole potentials were converted to relative RHE values. Linear sweep voltammetric (LSV) curves of the working electrode were first examined to determine the initial potential of electrochemical NO3⁻RR. The LSV curves of γ -CD and the γ -CD-K⁺ complex showed different current densities from -0.1 to -1.5 V and displayed significant improvement of the current density in the presence of NO₃⁻ compared with free 0.1 M KOH electrolyte alone, indicative of their catalytic activities for NO3⁻ electrochemical reduction (Figure 1a,d). It is worth mentioning that the γ -CD-K⁺ complex possessed a higher current density under the same conditions, suggesting its better electrocatalytic activity. The absorption curve of the electrolyte evidently confirmed the generation of the product NH₃, and such absorption intensity of the electrolyte increased when the potential gradually became negative (Figure S4). The illustration in Figure S4 (inset) shows color reactions of a series of electrolytes



Figure 1. LSV curves of (a) γ -CD and (d) the γ -CD-K⁺ complex in 0.1 M KOH electrolyte with and without nitrate. Chronoamperometric curves of (b) γ -CD and (e) the γ -CD-K⁺ complex at each given potential in 0.1 M KOH/0.1 M KNO₃ electrolyte. Potential-dependent FEs (left axis) and NH₃ yield rates (right axis) of (c) γ -CD and (f) the γ -CD-K⁺ complex in 0.1 M KOH/0.1 M KNO₃ electrolyte under ambient conditions.

collected after electrolysis under different applied voltages. The green color became deeper from left to right, indicative of the increasing concentration of produced $\rm NH_4^+$ in turn.

Subsequently, the produced NH₃ yield rates and FEs over the catalysts were quantitatively calculated. The NH4⁺ concentration is determined through the reported indophenol blue method. Time-dependent current density curves from -0.7 to -1.1 V for 1.0 h are shown in Figure 1b and e. Both NH₃ yield rate and FE uncovered that the parent γ -CD was an effective electrocatalyst for the conversion of NO₃⁻ into valueadded NH₃. The NH₃ yield rate gradually increased when the negative potential changed from -0.7 V to -1.1 V, in which the maximum NH₃ yield rate was measured to be 2.68 mg h^{-1} cm^{-2} at -1.1 V (Figure 1c). Moreover, the FE exhibited the highest value of 63.37% at -0.9 V followed by a gradual decline, which possibly originated from the competition of the hydrogen evolution reaction (HER). Furthermore, under the same conditions, compared with γ -CD, parent α -CD and β -CD presented relatively low NH₃ yield rates and FEs, whose values were 0.84 mg h^{-1} cm⁻²/43.91% at -0.8 V and 1.05 mg h^{-1} cm⁻²/55.05% at -0.9 V, respectively (Figure S5 and Figure S6). This was probably due to the difference of hydroxyl group numbers covering the exterior surface of the CDs. Moreover, we performed electrochemical control experiments by changing the Pt CE to a nonmetal electrode (reticulated vitreous carbon, RVC). The experimental results (Figures S7 and S8) showed that the RVC CE exhibited an effective FE and NH₃ yield rate (maximum values of 62.21% and 2.83 mg h^{-1} cm⁻² at -0.9 V vs RHE), which proved that the nitrate reduction reaction came from the real intrinsic catalytic activity of the γ -CD material rather than benefiting from the redeposited Pt. In addition, by the systematic analysis of the electrolytes and catalyst-coated electrodes before and after the reaction with SEM-EDX, XPS, and ICP-OES techniques (Tables S1-S7 and Figures S10-S13), it can be confirmed that there is no existence of any metal impurities (such as Pt, Fe, Ni, Cu, Co, and Ag) in our system. However, such a carbon-based CE is also unstable and easy to expand and break

due to oxygen gas generated from the anode during the electrocatalytic process, which can be readily observed from the blackening of the electrolyte (Figure S9). Therefore, we still choose a relatively stable platinum plate as the counter electrode for the investigation of the catalytic performance of materials in this work. For the case of the γ -CD-K⁺ complex (Figure 1f), the NH₃ yield rate and FE have been obviously improved in comparison to γ -CD, which was consistent with its relatively high time-dependent current density. The NH₃ yield rate increased with enhanced negative potential and reached a 6.63 mg h^{-1} cm⁻² peak at -1.1 V, proving that the coordination process participated by potassium ions playing an important role in the electrocatalytic reduction. However, an obvious volcano-shaped plot of FEs was observed for γ -CD-K⁺, with a maximum FE of 79.3% for NH₃ and the corresponding NH₃ yield rate of 4.66 mg h^{-1} cm⁻² at -0.9 V, indicating a fairly high electrocatalytic performance among the metal-free catalysts reported to the best of our knowledge (Table S8). These results also confirmed that the coordination of potassium can promote the further affinity for nitrate in the alkaline electrolyte, where the preorganized structure of γ -CD-K⁺ was more conducive to the efficient enrichment and electroreduction of nitrate. Since HER and NO3-RR are competitive reactions, H₂O molecules and NO₃⁻ ions have competitive adsorption on the electrode surface. A more negative potential might be more beneficial to H₂O surface adsorption, which is favorable to the HER. Figure S14 shows the potential-dependent FEs of the generated H_2 for γ -CD and γ -CD-K⁺, and γ -CD-K⁺ has better suppression ability for HER than γ -CD, especially at -0.9 V. The byproducts during the NO₃⁻RR process were also monitored. In addition to NH₃, nitrite-N was also generated, while the FE of nitrite-N was relatively low, at 6.4% and 5.6% for γ -CD and the γ -CD-K⁺ complex at -0.9 V, respectively, implying the favorable selectivity of NH_3 production (Figures S15–S17).

The electrocatalytic behavior of γ -CD in different electrolytes was also examined. Compared with an alkaline electrolyte (0.1 M KOH/0.1 M KNO₃, pH 13), the NH₃ yield rate and



Figure 2. (a) Corresponding NH₃ yield rates and FEs of γ -CD in three electrolytes. (b) Comparison of electrolyte counterion effect of Li⁺, Na⁺, and K⁺ on NH₃ yield rates and FEs of γ -CD. (c) Time-dependent current density curve of γ -CD during consecutive 12 h electrolysis. (d) The NH₃ yield rates over γ -CD in 0.1 M KOH electrolyte with different concentrations of KNO₃. Data are shown at -0.9 V versus RHE under ambient conditions.

FE of γ -CD are much higher than those in neutral electrolytes (0.1 M K₂SO₄/0.1 M KNO₃ or 0.1 M PBS/0.1 M KNO₃, pH 7) at -0.9 V, which suggested that KOH is expected to be an ideal electrolyte for electrochemical NO3-RR because of the inhibition of HER under alkaline conditions (Figure 2a). On the other hand, the result also implied that the alkaline medium is a necessary condition for deprotonation of γ -CD and coordination with K⁺. Moreover, a much smaller radius for γ -CD (Figure S18) was acquired from the electrochemical impedance spectroscopy (EIS) in the K⁺-containing electrolyte than in the Li⁺- and Na⁺-containing electrolytes, indicative of the relatively low interfacial charge transport resistance of γ -CD in the K⁺-involved alkaline electrolyte. Therefore, all the following NO₃-RR tests were performed in 0.1 M KOH with 0.1 M KNO₃. Next, the effect of alkali metal cations in an alkaline electrolyte on NO3-RR was also investigated. As shown in Figure 2b, γ -CD exhibited poor performance of NO₃⁻RR in an alkaline electrolyte composed of 0.1 M LiOH/ 0.1 M LiNO₃. However, the NH₃ yield rate and FE were markedly improved in the electrolytes dominated by potassium or sodium ions. Besides, the FE in 0.1 M KOH/0.1 M KNO₃ is slightly higher than that in 0.1 M NaOH/0.1 M NaNO₃. The reason for this phenomenon might come from the different migration rates caused by different ionic radii.43 Continuous recycling electrolysis at -0.9 V was performed to assess the electrochemical stability of γ -CD for NO₃-RR at room temperature, where the current density remains basically stable in 0.1 M KOH/0.1 M KNO3 in the course of electrolysis for 12 h (Figure 2c). In addition, the NH₃ yield rate and FE of γ -CD changed little after 5 cycles of electrochemical testing at -0.9

V (Figure S19). The above results showed that γ -CD has excellent stability and satisfactory electrocatalytic activity for NO₃⁻RR.

One of the advantages of CDs as electrocatalysts is that there is no interference of the nitrogen source. In order to further eliminate the possible interference of the external environment or other factors, a control experiment using γ -CD as working electrode in a blank 0.1 M KOH solution was carried out (Figure 2d). The results suggested that the formation of NH_3 over γ -CD was almost negligible in the 0.1 M KOH solution. Meanwhile, it was found that the corresponding ammonia yield rate on γ -CD also gradually increased when increasing the NO_3^- concentration in the electrolyte, which further confirmed that ammonia came from electrocatalytic NO₃⁻RR. Additionally, in order to further explore the origin of the generated ammonia, ¹⁵N isotope-labeling experiments were conducted. First, commercial ¹⁴NH₄Cl and ¹⁵NH₄Cl with 99% atomic abundance were used as standard samples to optimize the conditions of the NMR test, respectively. Whether it is ¹⁴NH₄Cl or ¹⁵NH₄Cl, the pH value of the sample strongly affected the signal intensity, which was caused by the proton exchange between the solvent and NH_4^+ (Figure 3a and b). Specifically, no significant signal was detected in samples with pH values of 6.0 and 7.0. For the sample with a pH value of 5.0, only one passivation signal was detected at 6.93 ppm. However, when the pH value of the sample is 4.0, three broad signals of ¹⁴NH₄Cl and two broad signals of ¹⁵NH₄Cl can be observed, respectively. When the pH value decreased from 4.0 to 2.0, the signals for both of them increased significantly, which indicated that the signal-to-noise



Figure 3. 1D ¹H NMR spectra of (a) standard ¹⁴NH₄Cl (99 atom %) and (b) standard ¹⁵NH₄Cl (99 atom %) at pH 2.0, 3.0, 4.0, 5.0, 6.0, and 7.0. ¹⁵N isotope-labeling experiments: (c) 1D ¹H NMR spectra of the electrolyte after electrocatalytic NO₃⁻RR over γ -CD using K¹⁵NO₃ (99 atom %) or K¹⁴NO₃ (99 atom %) as the nitrogen source and standard samples of ¹⁴NH₄Cl (99 atom %) or ¹⁵NH₄Cl (99 atom %) and (d) 1D ¹H NMR spectra of the electrolyte after electrocatalytic NO₃⁻RR over γ -CD using K¹⁵NO₃ (10 atom %) as the nitrogen source and the standard sample of ¹⁵NH₄Cl (10 atom %). The spectra were recorded at 298 K in ultrapure water containing 6% DMSO-*d*₆ at pH 2.0 by using a Bruker 400 MHz spectrometer with a cryoprobe.

ratio was higher with the decrease of pH value. Therefore, the isotope-labeling experiment was carried out under the optimized condition of pH 2.0.

The standard samples represented a triplet coupling of $^{14}\mathrm{NH_4^{\,+}}$ with the coupling constant of 52.3 Hz and a doublet coupling of ${}^{15}NH_4^+$ with the coupling constant of 73.2 Hz in the ¹H NMR spectrum in pH 2.0 solution, in which the coupling constants were consistent with the heteronuclear coupling constant of ¹⁴NH₄⁺ or ¹⁵NH₄⁺ between ¹H and ¹⁴N or ¹⁵N. Using γ -CD as the working electrode, the ¹H NMR spectrum of the electrolyte collected after electrocatalytic NO₃⁻RR displayed typical triplet peaks (6.81, 6.93, and 7.07 ppm) or doublet peaks (6.83 ppm, 7.01 ppm) when K¹⁴NO₃ (99 atom %) or K¹⁵NO₃ (99 atom %) was supplied as the nitrogen source, which was completely consistent with the standard samples of ¹⁴NH₄Cl (99 atom %) and ¹⁵NH₄Cl (99 atom %) (Figure 3c). Moreover, both triplet peaks and doublet peaks could be found in the ¹H NMR spectrum when using $K^{15}NO_3$ (10 atom %) as feeding nitrogen source, which also conformed to the peak pattern of the standard sample ¹⁵NH₄Cl (10 atom %) (Figure 3d). In addition, the same doublet and triplet peaks assigned to ¹⁵NH₄⁺ and ¹⁴NH₄⁺, respectively, were observed when K¹⁵NO₃ (99 atom %) and K¹⁴NO₃ (99 atom %) were used as feeding nitrogen sources for NO_3 -RR, further verifying the production of ammonia even if RVC and γ -CD were used as counter electrode and working electrode, respectively (Figure S20). These results jointly affirmed that the generated NH₃ indeed came from the electroreduction of nitrate over the γ -CD instead of other contaminants.

To further confirm the highly efficient electrocatalytic performance of purely organic CDs, we also prepared Rubased nanoporous carbon (denoted as Ru@C) as a control. First, the γ -CD-K⁺ complex containing [Ru(bpy)₃]Cl₂ was obtained by a cocrystallization strategy. Through the comparison of NMR spectra, it could be clearly found that $[Ru(bpy)_3]Cl_2$ was loaded into the cavity of the γ -CD-K⁺ complex (Figure S21). The $[Ru(bpy)_3]Cl_2/\gamma$ -CD-K+ complex still showed a cubic structure with strong red fluorescence from $[Ru(bpy)_3]Cl_2$ under confocal laser scanning microscopy (Figure S22). The standard absorption curve of $[Ru(bpy)_3]Cl_2$ with different concentrations at 453 nm is shown in Figure S23. The amount of $[Ru(bpy)_3]Cl_2$ in the γ -CD-K⁺ complex was determined as 1.04% per milligram by measuring the UV absorption per unit mass according to the standard curve (Figure S24). Next, nanoporous Ru@C based on this $[Ru(bpy)_3]Cl_2/\gamma$ -CD-K⁺ complex was subsequently synthesized under an argon atmosphere via direct carbonization at 850 °C. The morphology and composition of Ru@C were fully characterized by transmission electron microscopy (TEM) and scanning electron microscopy (SEM). TEM images showed an irregular lamellar structure at the micron level, suggesting that the uniformly shaped $[Ru(bpy)_3]Cl_2/\gamma$ -CD-K⁺ was destroyed and transformed into irregular amorphous carbon (Figure S25). More intuitively, Ru@C displayed a similar structural morphology, where its surface is smooth and flat, as indicated in SEM images (Figure S26). Moreover, the elemental mapping images for C, O, K, and Ru were also investigated for Ru@C by using EDX spectroscopy. Obviously, these four elements were highly distributed in Ru@C after calcination,



Figure 4. (a) Corresponding chemical structural formulas of permethyl- γ -CD, D-glucose, poly(vinyl alcohol), and γ -CD. (b) LSV curves of different samples in 0.1 M KOH/0.1 M KNO₃ electrolyte. (c) FEs and NH₃ yield rates of different samples under ambient conditions after 1 h of electrolysis in 0.1 M KOH/0.1 M KNO₃ electrolyte at -0.9 V vs RHE.

and the content of Ru was measured to be approximately 1.21% (atomic) by mapping analysis (Figure S27). The XRD pattern further revealed the formation of an amorphous structure of Ru@C (Figure S28).

A series of different materials were exploited and used for control experiments to further illustrate the mechanism of purely organic CDs for electrocatalytic NO₃⁻RR (Figure 4a). Negligible NH₃ could be detected at open-circuit potential, indicating that γ -CD could not spontaneously catalyze the nitrate reduction reaction. And the NH₃ yield rate could also be ignored when the working electrode was pristine carbon paper, which also ruled out the unreliable results caused by the possible Pt dissolution and redeposition when utilizing Pt as the counter electrode. For comparison, fully methylated permethyl- γ -CD was synthesized where the hydroxyl hydrogen of the parent γ -CD is substituted by methyl (Figure S29 and Figure S30), so the deprotonation process and effective coordination of potassium ions cannot be realized in alkaline solution. As expected, permethyl-7-CD exhibited a poor NH₃ yield rate as low as 0.04 mg h^{-1} cm⁻² with an FE of 1.48%. D-Glucose as a cyclodextrin structural unit and poly(vinyl alcohol) (PVA) containing alternating hydroxyl groups also showed disappointing FEs of less than 0.5% and NH₃ yield rates of less than 0.01 mg h^{-1} cm⁻². Moreover, we adopted the bare carbon paper as a working electrode and dispersed the cyclodextrin with the same catalyst loading into the alkaline electrolyte to investigate electrocatalytic NO₃⁻RR, which exhibited an inferior NH₃ yield rate of 0.06 mg h⁻¹ cm⁻²

with an FE of 6.79%. Such a catalytic effect might be caused by random collision and adsorption of γ -CD onto the carbon paper. The LSV curves of different samples indicated a consistent conclusion with the above analysis (Figure 4b) It is worth mentioning that the amorphous Ru@C doped with a noble metal showed a relatively high FE of 28.3% and NH₃ yield rate of 0.56 mg h⁻¹ cm⁻² but far less than those of parent γ -CD (Figure 4c). These control experiments showed that the hydroxyl group and inherent cavity structure of CDs played crucial roles in electrocatalytic nitrate reduction. Furthermore, ¹H NMR spectra of γ -CD after adding different equivalents of potassium nitrate were examined (Figure S31). The peak belonging to γ -CD gradually moved to low field after adding different equivalents of potassium nitrate, proving the interaction between the hydrogen of γ -CD and potassium nitrate.

The *in situ* Fourier transform infrared reflection (FTIR) measurement was also performed to capture adsorbed intermediates on the γ -CD catalyst surface to elucidate the chemical reaction mechanism of nitrate electroreduction. As seen in Figure S32, the bands at 1856 and 1904 cm⁻¹ could be ascribed to the weakly adsorbed NO,⁴⁴ and the bands at 1610 and 1214 cm⁻¹ corresponded to the stretching mode of NO₂^{-,45} suggesting successive deoxygenation steps during the NO₃⁻ reduction. Additionally, the bands at 1470 and 1266 cm⁻¹ could be assigned to H–N–H bending and NH₂ wagging bands,^{46,47} indicative of the substantial hydrogen generation for NH₃ evolution after deoxygenation. These *in*



Figure 5. Schematic illustration of the possible mechanism of the electrochemical nitrate reduction process catalyzed by γ -CD-K⁺.

situ FTIR results revealed that NO₃⁻RR proceeded via a threestep process with key nitrite and NO intermediates, namely, a NO₃⁻ \rightarrow NO₂⁻ \rightarrow NO \rightarrow NH₃ pathway.

The possible mechanism of the electrochemical nitrate reduction process catalyzed by γ -CD is shown in Figure 5. In KOH electrolyte solution, the coordination of K⁺ ions with hydroxyl groups in γ -CD induces the formation of extended 3D γ -CD-K⁺ frameworks with six CDs as a building unit.^{48–50} Such γ -CD-K⁺ frameworks containing the uncoordinated hydroxyl groups and the complexed K⁺ ions can act as cage nanoreactors to initiate NO3-RR. The uncoordinated edge hydroxyl groups within cage nanoreactors, as dominant catalytic sites, would effectively absorb and activate nitrate through hydrogen-bonding interactions to drive NO₃⁻RR.^{51,52} Besides, the electrostatic interaction through those complexed K⁺ ions confined within cage nanoreactors and NO₃⁻ also contributes to the enhanced enrichment effect of nitrate ions and promotes the mass transfer, thus realizing the highefficiency electroreduction of NO_3^- into NH_3 over the γ -CD-K⁺ complex under ambient conditions.

CONCLUSIONS

In summary, we utilized natural pure organic CDs as cathode materials to realize effective NO^{3–}RR with favorable FE and NH₃ yield rate at ambient pressure and room temperature especially in an alkaline electrolyte. α -, β -, and γ -CDs all exhibited efficient electrocatalytic performance, in which γ -CD can achieve an NH₃ yield rate up to 2.28 mg h⁻¹ cm⁻² with an FE of 63.2% at -0.9 V vs RHE on account of the distinctive torus-shaped cyclic structure of CDs, whose hydroxyl group has an affinity for anionic nitrate via a hydrogen-bonding interaction, thereby facilitating the electroreduction of nitrate over the electrode. Furthermore, the γ -CD-K⁺ complex can achieve a maximum NH₃ production rate up to 4.66 mg h⁻¹ cm⁻² with a high FE of 79.3%, in which the electrostatic interaction through K⁺ ions coordinated with hydroxyl groups also promotes the enrichment effect of NO₃⁻ ions and thus

further improves the performance of NO_3^-RR in an alkaline electrolyte. The current research shows that purely organic CDs can perform highly efficient electrocatalysis, which can avoid pollution to the environment such as soil and water resources compared with metal catalysts as well as offer a very important approach for an environmentally friendly electrochemical nitrate reduction reaction.

EXPERIMENTAL SECTION

Cathode Preparation. First, the carbon paper was cut into 1.0 cm \times 2.0 cm in size, then cleaned ultrasonically with 0.1 mol L⁻¹ hydrochloric acid, acetone, ethanol, and deionized water, and finally dried at 60 °C for standby. Concretely, 10 μ L of Nafion solution (5 wt %) with 6.0 mg of catalyst was dispersed in isopropanol (590 μ L) followed by sonicating for 30 min until a homogeneous ink formed. Subsequently, a carbon paper with an area of 1.0 \times 1.0 cm² (1 mg cm⁻²) loading 100 μ L of homogeneous ink was dried under ambient conditions.

Electrochemical Measurement. Typically, the electrocatalytic NO_3 ¬RR was examined in the standard three-electrode system, in which an H-type sealed double chamber was used as the electrolytic cell, cyclodextrin-loaded carbon paper was used as the working electrode, a platinum plate served as the counter electrode, Ag/AgCl was the reference electrode, and a 0.1 M KOH and KNO₃ solution served as the electrolyte. The Nafion membrane was heated at 80 °C in 5% H₂O₂ solution and deionized water for 1 h to remove possible impurities before the test. For comparison, the nonmetal RVC electrode as the counter electrode was also used to exclude the influence of the possible Pt dissolution and redeposition on the electrocatalytic performance. The potential values are converted to relative RHE on the basis of the following equation:

 $E_{\rm RHE} = E_{\rm Ag/AgCl} + 0.059 \rm{pH} + 0.197$

The potentiostat tests were performed at different potentials for 1 h. The potentials were -0.7, -0.8, -0.9, -1.0, and -1.1 V, respectively. After 1 h of electrolysis, the electrolyte from the cathode of the electrolytic cell was collected, and then the new electrolyte was added after each electrolysis. All electrochemical tests were conducted at room temperature (25 ± 2 °C).

v

Determination of Ammonia. NH₃ produced by electrocatalysis was quantitatively determined based on the indophenol blue colorimetry method by employing reagents with the highest available purity. First, in order to ensure that the NH₂ concentration in the electrolyte was within the linear range, deionized water was utilized to dilute the electrolytes obtained after catalysis at different potentials for 1 h. Then 2.0 mL of a 1 M NaOH solution containing 5 wt % salicylic acid and 5 wt % sodium citrate was successively added to the above solution, followed by addition of 1.0 mL of 0.05 M NaClO and 200 μ L of 1 wt % C₅FeN₆Na₂O (sodium nitroso ferricyanide) aqueous solutions. The mixed solution was allowed to stand at room temperature and away from light for 2 h to ensure complete coloring reaction. The concentration of NH3 was acquired based on the absorbance at 656 nm. By using a known concentration of ammonium chloride solution as the standard, the absolute calibration of the method was realized. The concentration-absorbance standard curve of a NH₄Cl solution was established according to the absorbance of the standard solution at 656 nm.

Determination of Nitrite-N. Typically, ultrapure water (50 mL) and phosphoric acid (10 mL, $\rho = 1.70$ g/mL) with *N*-(1-naphthyl) ethylenediamine dihydrochloride (0.2 g) and *p*-aminobenzene-sulfonamide (4.0 g) were mixed together to obtain the color reagent. An appropriate amount of electrolyte was taken out from the electrolytic cell and diluted it to 5 mL with the detection range; then the color reagent (0.1 mL) was added into 5 mL of the aforementioned solution with homogeneously mixing, and finally the absorbance at 540 nm was monitored after aging for 20 min.

Determination of the Gas Product H₂. With Ar as the carrier gas, an online gas chromatograph (FULI 9790) was adopted to detect the gas products. This gas chromatograph was equipped with a thermal conductivity detector (TCD) and a MolSieve 5A column. The generated H₂ was quantified on a gas chromatograph (GC 2014 Shimadzu) with Porapak N and MolSieve 5 Å columns leading to a TCD.

Faradaic efficiency of the generated H_2 was calculated using the following equation:

$$FE_{H_2} = \frac{n_{H_2} \times z \times F}{Q} \times 100\%$$

where n_{H_2} is the moles of the formed H₂; z is the electron transfer number, $z_{H_2} = 2$; Q is the charge consumption during the reaction; and F is the Faradaic constant (96485 C·mol⁻¹).

Preparation of the γ -CD-K⁺ Complex from the Vapor Diffusion Method. KOH (0.45 g, 8 mmol) and γ -CD (1.30 g, 1 mmol) were dissolved in distilled water (20 mL). A 0.45 μ m microporous filter membrane was used to filter the above aqueous solution, and then MeOH was allowed to evaporate and diffuse into the above solution. After 3 days, white cubic crystals appearing at the bottom of the vessel were separated, filtered, and washed three times with MeOH, which were further dried in a vacuum oven to obtain the white power (denoted as γ -CD-K⁺).

Preparation of Ru@C. During a typical synthetic procedure for the γ-CD-K⁺ complex, 560 mg of γ-CD and 260 mg of KOH were dissolved in 10 mL of deionized water. The obtained solution was filtered by a 0.45 µm filter membrane, and then methanol was allowed to evaporate and diffuse into the solution. After 5 days, transparent cubic crystals appeared on the bottle wall and bottom and were isolated, filtered, and washed with MeOH three times. The final sample was obtained by vacuum drying at 45 °C for 12 h. The preparation of [Ru(bpy)₃]Cl₂/γ-CD-K⁺ was the same as above except that an additional 80.0 mg of [Ru(bpy)₃]Cl₂ was added into the aqueous solution before evaporation and diffusion. Ru@C was obtained by carbonization of the prepared [Ru(bpy)₃]Cl₂/γ-CD-K⁺ in a tube furnace under an argon atmosphere at 850 °C for 5 h with a heating rate of 5 °C min⁻¹.

Calculation of NH₃ Faradaic Efficiency and NH₃ Yield Rate. The NH₃ yield rate is calculated according to the following formula:

$$_{\rm NH_3} = \frac{V_{\rm catholyte} \times C_{\rm NH_3}}{A \times t}$$

The Faraday efficiency of NH_3 is calculated by the following equation:

Faraday efficiency =
$$\frac{nF \times V_{\text{catholyte}} C_{\text{NH}_3}}{Q}$$

where *n* represents the number of transferred electrons when 1 mol of NH₃ is formed. $V_{\text{catholyte}}$ is the volume of the cathodal electrolyte (unit: mL), C_{NH_3} is the detected NH₃ concentration (unit: $\mu \text{g mL}^{-1}$), *t* is the electrolysis time (unit: h), *A* is the geometric area of the electrode immersed in the solution (unit: cm²), *F* is the Faraday constant (96 485 C mol⁻¹), and *Q* is the applied electric quantity (unit: C).

Isotope-Labeling Experiments. In order to optimize the testing conditions of nuclear magnetic resonance (NMR), a series of $^{14}\mathrm{NH_4Cl}$ (99 atom %, 5 mg/mL) or $^{15}\mathrm{NH_4Cl}$ (99 atom %, 5 mg/ mL) solutions with different pH values (2.0, 3.0, 4.0, 5.0, 6.0, 7.0) were prepared in ultrapure water containing 6% DMSO- d_6 (v/v). For each sample, the pH value was regulated by employing 4 M HCl and 4 M NaOH aqueous solutions. Then the NMR measurements were carried out on a Bruker Avance 400 MHz (¹H frequency) spectrometer equipped with a cryoprobe at 298 K with a number of scans of 64. In the following isotope labeling experiments, ¹⁴NH₄Cl (99 atom %, 5 mg/mL) or $^{15}NH_4Cl$ (99 atom %, 5 mg/mL) solutions at pH = 2 were used as standard samples. K¹⁴NO₃ (99 atom %) or K¹⁵NO₃ (99 atom %) was used as a nitrogen source for electrocatalytic nitrate reduction experiments, respectively, which were conducted at -0.9 V vs RHE for 5 h in a 30 mL aqueous solution with 0.1 M KOH and K¹⁴NO₃ or K¹⁵NO₃. The process of the isotope labeling test is described as above.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsnano.2c06441.

FTIR spectra and XRD patterns (Figures S1 and S2), quantification of ammonia in the electrolyte and corresponding UV-vis adsorption spectra (Figures S3 and S4), potential-dependent Faradaic efficiencies and ammonia yields (Figures S5-S9), characterizations including SEM, EDX, XPS, and ICP-OES of working electrode or electrolytes (Figures S10-S13 and Tables S1-S8), potential-dependent Faradaic efficiencies of the generated H₂ and nitrite-N (Figures S14-S17), electrochemical impedance spectra, recycling test, and isotopelabeling ¹H NMR spectra (Figures S18-S20), characterizations of $[Ru(bpy)_3]Cl_2/\gamma$ -CD-K⁺ (Figures S21–S28), ¹H NMR and ¹³C NMR spectra of permethyl-γ-CD (Figures S29 and S30), ¹H NMR spectral changes of γ -CD with potassium nitrate and in situ Fourier transform infrared reflection spectroscopy (Figures S31 and S32) (PDF)

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Notes

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REFERENCES

(1) Gruber, N.; Galloway, J. N. An Earth-system perspective of the global nitrogen cycle. *Nature* **2008**, *451*, 293–296.

(2) Cheng, H.; Ding, L.-X.; Chen, G.-F.; Zhang, L.; Xue, J.; Wang, H. Molybdenum Carbide Nanodots Enable Efficient Electrocatalytic Nitrogen Fixation under Ambient Conditions. *Adv. Mater.* **2018**, *30*, 1803694.

(3) Foster, S. L.; Bakovic, S. I. P.; Duda, R. D.; Maheshwari, S.; Milton, R. D.; Minteer, S. D.; Janik, M. J.; Renner, J. N.; Greenlee, L. F. Catalysts for nitrogen reduction to ammonia. *Nat. Catal.* **2018**, *1*, 490–500.

(4) Tang, C.; Qiao, S.-Z. How to explore ambient electrocatalytic nitrogen reduction reliably and insightfully. *Chem. Soc. Rev.* **2019**, *48*, 3166–3180.

(5) Chen, J. G.; Crooks, R. M.; Seefeldt, L. C.; Bren, K. L.; Bullock, R. M.; Darensbourg, M. Y.; Holland, P. L.; Hoffman, B.; Janik, M. J.; Jones, A. K.; Kanatzidis, M. G.; King, P.; Lancaster, K. M.; Lymar, S. V.; Pfromm, P.; Schneider, W. F.; Schrock, R. R. Beyond fossil fueldriven nitrogen transformations. *Science* **2018**, *360*, eaar6611.

(6) Suryanto, B. H. R.; Du, H.-L.; Wang, D.; Chen, J.; Simonov, A. N.; MacFarlane, D. R. Challenges and prospects in the catalysis of electroreduction of nitrogen to ammonia. *Nat. Catal.* **2019**, *2*, 290–296.

(7) Hawtof, R.; Ghosh, S.; Guarr, E.; Xu, C. Y.; Sankaran, R. M.; Renner, J. N. Catalyst-free, highly selective synthesis of ammonia from nitrogen and water by a plasma electrolytic system. *Sci. Adv.* **2019**, *5*, eaat5778.

(8) Ma, Y.; Yang, T.; Zou, H.; Zang, W.; Kou, Z.; Mao, L.; Feng, Y.; Shen, L.; Pennycook, S. J.; Duan, L.; Li, X.; Wang, J. Synergizing Mo Single Atoms and Mo₂C Nanoparticles on CNTs Synchronizes Selectivity and Activity of Electrocatalytic N₂ Reduction to Ammonia. *Adv. Mater.* **2020**, *32*, 2002177.

(9) Lv, C.; Yan, C.; Chen, G.; Ding, Y.; Sun, J.; Zhou, Y.; Yu, G. An Amorphous Noble-Metal-Free Electrocatalyst that Enables Nitrogen Fixation under Ambient Conditions. Angew. Chem., Int. Ed. 2018, 57, 6073–6076.

(10) Seh, Z. W.; Kibsgaard, J.; Dickens, C. F.; Chorkendorff, I.; Nørskov, J. K.; Jaramillo, T. F. Combining theory and experiment in electrocatalysis: Insights into materials design. *Science* **2017**, *355*, eaad4998.

(11) Cui, X.; Tang, C.; Zhang, Q. A Review of Electrocatalytic Reduction of Dinitrogen to Ammonia under Ambient Conditions. *Adv. Energy Mater.* **2018**, *8*, 1800369.

(12) van der Ham, C. J. M.; Koper, M. T. M.; Hetterscheid, D. G. H. Challenges in reduction of dinitrogen by proton and electron transfer. *Chem. Soc. Rev.* **2014**, *43*, 5183–5191.

(13) Wang, J.; Yu, L.; Hu, L.; Chen, G.; Xin, H.; Feng, X. Ambient ammonia synthesis via palladium-catalyzed electrohydrogenation of dinitrogen at low overpotential. *Nat. Commun.* **2018**, *9*, 1795.

(14) Wang, Y.; Xu, A.; Wang, Z.; Huang, L.; Li, J.; Li, F.; Wicks, J.; Luo, M.; Nam, D.-H.; Tan, C.-S.; Ding, Y.; Wu, J.; Lum, Y.; Dinh, C.-T.; Sinton, D.; Zheng, G.; Sargent, E. H. Enhanced Nitrate-to-Ammonia Activity on Copper–Nickel Alloys via Tuning of Intermediate Adsorption. J. Am. Chem. Soc. **2020**, *142*, 5702–5708.

(15) Wang, Y.; Zhou, W.; Jia, R.; Yu, Y.; Zhang, B. Unveiling the Activity Origin of a Copper-based Electrocatalyst for Selective Nitrate Reduction to Ammonia. *Angew. Chem., Int. Ed.* 2020, 59, 5350–5354.
(16) Liu, Y.; Wang, J. Reduction of nitrate by zero valent iron (ZVI)-

based materials: A review. *Sci. Total Environ.* **2019**, *671*, 388–403. (17) Wang, Y.; Wang, C.; Li, M.; Yu, Y.; Zhang, B. Nitrate electroreduction: mechanism insight, in situ characterization, performance evaluation, and challenges. *Chem. Soc. Rev.* **2021**, *50*, 6720–6733.

(18) Wang, Y.; Yu, Y.; Jia, R.; Zhang, C.; Zhang, B. Electrochemical synthesis of nitric acid from air and ammonia through waste utilization. *Nat. Sci. Rev.* **2019**, *6*, 730–738.

(19) Zhang, X.; Wang, Y.; Liu, C.; Yu, Y.; Lu, S.; Zhang, B. Recent advances in non-noble metal electrocatalysts for nitrate reduction. *Chem. Eng. J.* **2021**, 403, 126269.

(20) Su, L.; Han, D.; Zhu, G.; Xu, H.; Luo, W.; Wang, L.; Jiang, W.; Dong, A.; Yang, J. Tailoring the Assembly of Iron Nanoparticles in Carbon Microspheres toward High-Performance Electrocatalytic Denitrification. *Nano Lett.* **2019**, *19*, 5423–5430.

(21) Wu, Z.-Y.; Karamad, M.; Yong, X.; Huang, Q.; Cullen, D. A.; Zhu, P.; Xia, C.; Xiao, Q.; Shakouri, M.; Chen, F.-Y.; Kim, J. Y.; Xia, Y.; Heck, K.; Hu, Y.; Wong, M. S.; Li, Q.; Gates, I.; Siahrostami, S.; Wang, H. Electrochemical ammonia synthesis via nitrate reduction on Fe single atom catalyst. *Nat. Commun.* **2021**, *12*, 2870.

(22) Zhao, S.; Lu, X.; Wang, L.; Gale, J.; Amal, R. Carbon-Based Metal-Free Catalysts for Electrocatalytic Reduction of Nitrogen for Synthesis of Ammonia at Ambient Conditions. *Adv. Mater.* **2019**, *31*, 1805367.

(23) Zhang, L.; Ding, L. X.; Chen, G. F.; Yang, X.; Wang, H. Ammonia Synthesis Under Ambient Conditions: Selective Electroreduction of Dinitrogen to Ammonia on Black Phosphorus Nanosheets. *Angew. Chem., Int. Ed.* **2019**, *58*, 2612–2616.

(24) Liu, S.; Wang, M.; Qian, T.; Ji, H.; Liu, J.; Yan, C. Facilitating nitrogen accessibility to boron-rich covalent organic frameworks via electrochemical excitation for efficient nitrogen fixation. *Nat. Commun.* **2019**, *10*, 3898.

(25) Qiu, W.; Xie, X.-Y.; Qiu, J.; Fang, W.-H.; Liang, R.; Ren, X.; Ji, X.; Cui, G.; Asiri, A. M.; Cui, G.; Tang, B.; Sun, X. High-performance artificial nitrogen fixation at ambient conditions using a metal-free electrocatalyst. *Nat. Commun.* **2018**, *9*, 3485.

(26) Liu, Y.; Su, Y.; Quan, X.; Fan, X.; Chen, S.; Yu, H.; Zhao, H.; Zhang, Y.; Zhao, J. Facile Ammonia Synthesis from Electrocatalytic N₂ Reduction under Ambient Conditions on N-Doped Porous Carbon. *ACS Catal.* **2018**, *8*, 1186–1191.

(27) Li, Y.; Xiao, S.; Li, X.; Chang, C.; Xie, M.; Xu, J.; Yang, Z. A robust metal-free electrocatalyst for nitrate reduction reaction to synthesize ammonia. *Mater. Today Phys.* **2021**, *19*, 100431.

(28) Alsbaiee, A.; Smith, B. J.; Xiao, L.; Ling, Y.; Helbling, D. E.; Dichtel, W. R. Rapid removal of organic micropollutants from water by a porous β -cyclodextrin polymer. *Nature* **2016**, *529*, 190–194.

(29) Zhang, Y. M.; Liu, Y. H.; Liu, Y. Cyclodextrin-Based Multistimuli-Responsive Supramolecular Assemblies and Their Biological Functions. *Adv. Mater.* **2020**, *32*, 1806158.

(30) Hu, S. S.; Li, J. Y.; Xiang, J. F.; Pan, J.; Luo, S. Z.; Cheng, J. P. Asymmetric Supramolecular Primary Amine Catalysis in Aqueous Buffer: Connections of Selective Recognition and Asymmetric Catalysis. J. Am. Chem. Soc. 2010, 132, 7216–7228.

(31) Chen, X.-Y.; Chen, H.; Đorđević, L.; Guo, Q.-H.; Wu, H.; Wang, Y.; Zhang, L.; Jiao, Y.; Cai, K.; Chen, H.; Stern, C. L.; Stupp, S. I.; Snurr, R. Q.; Shen, D.; Stoddart, J. F. Selective Photodimerization in a Cyclodextrin Metal–Organic Framework. *J. Am. Chem. Soc.* **2021**, *143*, 9129–9139.

(32) Breslow, R.; Dong, S. D. Biomimetic reactions catalyzed by cyclodextrins and their derivatives. *Chem. Rev.* 1998, 98, 1997–2011.
(33) Takahashi, K. Organic reactions mediated by cyclodextrins. *Chem. Rev.* 1998, 98, 2013–2033.

(34) Qiu, Z.-J.; Fan, S.-T.; Xing, C.-Y.; Song, M.-M.; Nie, Z.-J.; Xu, L.; Zhang, S.-X.; Wang, L.; Zhang, S.; Li, B.-J. Facile Fabrication of an AIE-Active Metal–Organic Framework for Sensitive Detection of Explosives in Liquid and Solid Phases. *ACS Appl. Mater. Interfaces* **2020**, *12*, 55299–55307.

(35) Gassensmith, J. J.; Kim, J. Y.; Holcroft, J. M.; Farha, O. K.; Stoddart, J. F.; Hupp, J. T.; Jeong, N. C. A Metal–Organic Framework-Based Material for Electrochemical Sensing of Carbon Dioxide. J. Am. Chem. Soc. **2014**, 136, 8277–8282.

(36) Wang, L.; Liang, X.-Y.; Chang, Z.-Y.; Ding, L.-S.; Zhang, S.; Li, B.-J. Effective Formaldehyde Capture by Green Cyclodextrin-Based Metal–Organic Framework. ACS ACS Appl. Mater. Interfaces 2018, 10, 42–46.

(37) Xu, L.; Xing, C.-Y.; Ke, D.; Chen, L.; Qiu, Z.-J.; Zeng, S.-L.; Li, B.-J.; Zhang, S. Amino-Functionalized β -Cyclodextrin to Construct Green Metal–Organic Framework Materials for CO2 Capture. ACS Appl. Mater. Interfaces **2020**, *12*, 3032–3041.

(38) Gassensmith, J. J.; Furukawa, H.; Smaldone, R. A.; Forgan, R. S.; Botros, Y. Y.; Yaghi, O. M.; Stoddart, J. F. Strong and Reversible Binding of Carbon Dioxide in a Green Metal–Organic Framework. *J. Am. Chem. Soc.* **2011**, *133*, 15312–15315.

(39) Hartlieb, K. J.; Holcroft, J. M.; Moghadam, P. Z.; Vermeulen, N. A.; Algaradah, M. M.; Nassar, M. S.; Botros, Y. Y.; Snurr, R. Q.; Stoddart, J. F. CD-MOF: A Versatile Separation Medium. J. Am. Chem. Soc. 2016, 138 (7), 2292–2301.

(40) Holcroft, J. M.; Hartlieb, K. J.; Moghadam, P. Z.; Bell, J. G.; Barin, G.; Ferris, D. P.; Bloch, E. D.; Algaradah, M. M.; Nassar, M. S.; Botros, Y. Y.; Thomas, K. M.; Long, J. R.; Snurr, R. Q.; Stoddart, J. F. Carbohydrate-Mediated Purification of Petrochemicals. *J. Am. Chem. Soc.* **2015**, *137* (17), 5706–5719.

(41) Zhang, C.-C.; Liu, X.; Liu, Y.-P.; Liu, Y. Two-Dimensional Supramolecular Nanoarchitectures of Polypseudorotaxanes Based on Cucurbit[8]uril for Highly Efficient Electrochemical Nitrogen Reduction. *Chem. Mater.* **2020**, *32* (19), 8724–8732.

(42) Smaldone, R. A.; Forgan, R. S.; Furukawa, H.; Gassensmith, J. J.; Slawin, A. M. Z.; Yaghi, O. M.; Stoddart, J. F. Metal-Organic Frameworks from Edible Natural Products. *Angew. Chem., Int. Ed.* **2010**, *49* (46), 8630–8634.

(43) Song, Y.; Johnson, D.; Peng, R.; Hensley, D. K.; Bonnesen, P. V.; Liang, L. B.; Huang, J. S.; Yang, F. C.; Zhang, F.; Qiao, R.; Baddorf, A. P.; Tschaplinski, T. J.; Engle, N. L.; Hatzell, M. C.; Wu, Z. L.; Cullen, D. A.; Meyer, H. M.; Sumpter, B. G.; Rondinone, A. J. A physical catalyst for the electrolysis of nitrogen to ammonia. *Sci. Adv.* **2018**, *4*, e1700336.

(44) Li, Q.; Gu, H.; Li, P.; Zhou, Y.; Liu, Y.; Qi, Z.; Xin, Y.; Zhang, Z. In situ IR studies of selective catalytic reduction of NO with NH3 on Ce-Ti amorphous oxides. *Chin. J. Catal.* **2014**, 35 (8), 1289–1298. (45) Zhang, N.; Shang, J.; Deng, X.; Cai, L.; Long, R.; Xiong, Y.; Chai, Y. Governing Interlayer Strain in Bismuth Nanocrystals for

Efficient Ammonia Electrosynthesis from Nitrate Reduction. ACS Nano 2022, 16 (3), 4795–4804.

(46) Yao, Y.; Zhu, S.; Wang, H.; Li, H.; Shao, M. A Spectroscopic Study of Electrochemical Nitrogen and Nitrate Reduction on Rhodium Surfaces. *Angew. Chem., Int. Ed.* **2020**, *59* (26), 10479–10483.

(47) Song, P.; Wang, H.; Kang, L.; Ran, B.; Song, H.; Wang, R. Electrochemical nitrogen reduction to ammonia at ambient conditions on nitrogen and phosphorus co-doped porous carbon. *Chem. Commun.* **2019**, *55* (5), 687–690.

(48) Roy, I.; Stoddart, J. F. Cyclodextrin Metal-Organic Frameworks and Their Applications. Acc. Chem. Res. 2021, 54 (6), 1440–1453.

(49) Xu, W.; Wang, L.-H.; Chen, Y.; Liu, Y. Flexible carbon membrane supercapacitor based on γ -cyclodextrin-MOF. *Mater. Today Chem.* **2022**, *24*, 100896.

(50) Liu, Z.; Liu, Y. Multicharged cyclodextrin supramolecular assemblies. *Chem. Soc. Rev.* **2022**, *51* (11), 4786–4827.

(51) Song, Z.; Liu, Y.; Zhong, Y.; Guo, Q.; Zeng, J.; Geng, Z. Efficient Electroreduction of Nitrate into Ammonia at Ultralow Concentrations Via an Enrichment Effect. *Adv. Mater.* **2022**, *34* (36), 2204306.

(52) Deng, W.; Zhang, L.; Li, L.; Chen, S.; Hu, C.; Zhao, Z.-J.; Wang, T.; Gong, J. Crucial Role of Surface Hydroxyls on the Activity and Stability in Electrochemical CO₂ Reduction. *J. Am. Chem. Soc.* **2019**, *141* (7), 2911–2915.

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