available at www.sciencedirect.com

journal homepage: www.elsevier.com/locate/chnjc

Article

Nitrogen and sulfur dual-doped high-surface-area hollow carbon nanospheres for efficient CO₂ reduction

Guodong Li^{a,b}, Yongjie Qin^b, Yu Wu^{a,b}, Lei Pei^b, Qi Hu^b, Hengpan Yang^b, Qianling Zhang^b, Jianhong Liu^b, Chuanxin He^{b,*}^a Department of Chemical Physics, University of Science and Technology of China, Hefei 230026, Anhui, China^b Shenzhen Key Laboratory for Functional Polymer, College of Chemistry and Environmental Engineering, Shenzhen University, Shenzhen 518060, Guangdong, China

ARTICLE INFO

Article history:

Received 25 September 2019

Accepted 29 October 2019

Published 5 May 2020

Keywords:

High specific surface area

Hollow structure

Carbon-based catalysts

CO₂ reduction reaction

Electrocatalytic selectivity

ABSTRACT

The electrochemical reduction of CO₂ (CO₂RR) can substantially contribute to the production of useful chemicals and reduction of global CO₂ emissions. Herein, we presented N and S dual-doped high-surface-area carbon materials (SZ-HCN) as CO₂RR catalysts. N and S were doped by one-step pyrolysis of a N-containing polymer and S powder. ZnCl₂ was applied as a volatile porogen to prepare porous SZ-HCN. SZ-HCN with a high specific surface area (1510 m² g⁻¹) exhibited efficient electrocatalytic activity and selectivity for CO₂RR. Electrochemical measurements demonstrated that SZ-HCN showed excellent catalytic performance for CO₂-to-CO reduction with a high CO Faradaic efficiency (~93%) at -0.6 V. Furthermore, SZ-HCN offered a stable current density and high CO selectivity over at least 20 h continuous operation, revealing remarkable electrocatalytic durability. The experimental results and density functional theory calculations indicated that N and S dual-doped carbon materials required lower Gibbs free energy to form the COOH* intermediate than that for single-N-doped carbon for CO₂-to-CO reduction, thereby enhancing CO₂RR activity.

© 2020, Dalian Institute of Chemical Physics, Chinese Academy of Sciences.

Published by Elsevier B.V. All rights reserved.

1. Introduction

Over the past several decades, fossil fuels have underpinned the global energy, leading to the ever-growing concentration of CO₂ in the atmosphere [1]. Among CO₂ conversion approaches, the electrocatalytic CO₂ reduction reaction (CO₂RR) into valuable chemicals or fuels has been widely considered as a promising carbon-neutral route for suitable and capable catalytic techniques [2–4]. However, the applicability of CO₂RR is limited because of the high kinetic barriers and the inevitable competition with the hydrogen evolution reaction (HER) [5–7].

Numerous catalysts have been extensively investigated for

CO₂RR, such as noble metals (e.g., Ag, Au, Pt, and Pd) [8–11], alloys (Pt-Au, Au-Cu, and Pd-Sn) [12–14], metal oxides (CuO, SnO₂, and Bi₂O₃) [15–17], and metallic complexes (Ru, Ir, and Pd complexes) [18–20]. These electrocatalysts are capable of reducing CO₂ to various products through a multi-electron transfer process, including CO, HCOOH, CH₄, high-order hydrocarbons, and oxygenates [21–23]. Among these products, CO has attracted considerable attention as an important feedstock for the production of liquid hydrocarbons via the well-known Fischer–Tropsch process [24,25]. For the conversion of CO₂ to CO, noble metals (e.g., Au, Ag, and Pd) as catalysts have demonstrated excellent activity and high selectivity of CO₂RR [26–28].

* Corresponding author. Tel: +86-0755-26534173; Fax: +86-755-26536141; E-mail: hecx@szu.edu.cn

This work was supported by the National Natural Science Foundation of China (21574084, 21571131), the Natural Science Foundation of Guangdong (2017A040405066), and Shenzhen Government's Plan of Science and Technology (JCYJ20160308104704791, JCYJ20170818091657056).

DOI: S1872-2067(19)63485-6 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 41, No. 5, May 2020

However, high cost, low stability, and potential environmental toxicity limit the large-scale application of noble metal catalysts. Recently, metal-free carbon materials have been explored as alternative catalysts for CO₂-to-CO reduction because of their low cost, tunable porous structures, high surface area, and easy incorporation of heteroatoms [29–31]. For instance, heteroatom-doped graphene, carbon fibers, carbon nanotubes, nanoporous carbon, and diamond materials exhibit CO₂RR activity and stability comparable to those of noble metals [32–36]. Among these materials, nanoporous carbon with characteristic features such as controlled nanostructures and high specific surface (SSA) and porosity may facilitate mass transport and abundant active sites in the CO₂RR process [37–40]. Although conventional approaches have been widely employed for the synthesis of nanoporous carbon (hard template, soft template, and activation methods), these methods offer certain disadvantages, such as the use of hazardous chemicals (hydrofluoric acid or hot alkaline solution) and time-consuming process [41–44]. In addition, the incorporation of heteroatoms (N, B, S and P) into porous carbon could result in asymmetric electron spin density and charge redistribution, which could increase intrinsic activity [45–50]. Therefore, the development of a useful and accessible route to obtain high-surface-area porous heteroatom-doped carbon materials and efficient electrocatalytic performance toward CO₂RR is still desirable.

Herein, a facile and effective strategy is developed for synthesizing N, S dual-doped high-surface-area hollow carbon materials (denoted as SZ-HCN) by one-step pyrolysis of a N-doped polymer and S powder. The hollow structure was achieved through the micelle-template-induced copolymerization of aniline and pyrrole monomer. Sulfuration was adopted to achieve dual-doping of N and S. In addition, ZnCl₂ salts as porogens were pivotal in the formation of the high-surface-area porous structure. Notably, hollow and porous structures with homogeneously effective N/S doping could be beneficial for CO₂RR activity arising from the enhanced accessibility of active sites and mass transport of related species. Because of these favorable characteristics, SZ-HCN could exhibit excellent CO₂RR activity and high CO Faradaic efficiency (~93%), outcompeting the catalysts for the competitive HER. Furthermore, SZ-HCN could maintain high efficiencies for at least 20 h durability tests. This simple strategy advances the development of efficient and robust carbon-based catalysts for a natural carbon cycle.

2. Experimental

2.1. Chemicals

All reagents were used without any further purification. Ultrapure water with a resistivity of >18 MΩ cm⁻¹ was used in all experiments.

2.2. Synthesis and preparation

A total of 0.06 g Triton X-100 was dispersed in 60 ml deionized water. Next, 0.4 g aniline and 0.3 g pyrrole were slowly

dropped into this solution. After 30 min magnetic stirring and 30 min ultrasonication, a homogeneous solution was obtained. A precooled aqueous solution of 2.0 g ammonium persulfate (APS) and 2.0 g ZnCl₂ (volatile porogen) in 10 mL H₂O were added to the mixed solution in one portion. The polymerization reaction was carried out at 0–2 °C under a static condition for 12 h. The obtained product was washed with ethanol and deionized water for several times and dried under vacuum at 60 °C for 24 h, forming polyaniline-co-polypyrrole (PACP) hollow carbon nanospheres. At the same time, ZnCl₂ diffuses onto PACP nanospheres (denoted PACP-Zn) at various positions. The as-prepared PACP-Zn (0.1 g) and 2.0 g of S powder were placed in a porcelain boat and calcined at 900 °C under argon atmosphere for 2 h. The obtained carbon material was denoted as SZ-HCN. For comparison, PACP nanospheres were synthesized by the polymerization of aniline and pyrrole without the addition of ZnCl₂. Moreover, PACP solid nanospheres were synthesized by the polymerization of aniline and pyrrole without the addition of Triton X-100 as a reference. The CN (without Triton X-100, ZnCl₂, and sulfur), HCN (without ZnCl₂ and sulfur), Z-HCN (without sulfur) and S-HCN (without ZnCl₂) samples were directly calcined at 900 °C under argon atmosphere for 2 h.

2.3. Characterization

The morphology and structure were characterized by field emission scanning electron microscopy (SEM, FEI JEOL-7800F) and transmission electron microscopy (TEM, JEM-2100F). A Raman spectrum was obtained by a Raman spectrometer (Rennishaw In Via) with a 514.5 nm laser excitation. X-ray photoelectron spectroscopy (XPS) was performed by an X-ray photoelectron spectrometer (Thermo VG Scientific ESCALAB 250, Thermo Electron, U.K.) with Al K_α X-ray radiation. The binding energies were calibrated on the basis of C 1s peak (284.8 eV). X-ray powder diffraction (XRD) patterns were acquired by an X-ray diffractometer (Rigaku Mini Flex 600) with Cu K_α radiation (λ = 0.15418 nm) in the range from 10° to 80°. N₂ adsorption/desorption isotherms were obtained by an ASAP 2460 system (Micromeritics) at 77 K.

2.4. Electrochemical measurements

Electrochemical measurements were carried out on a three-electrode system with an electrochemical station (CHI 760E, CH Instrument Inc). The CO₂ electroreduction products were analyzed by gas chromatography (SRI 8610C). Electrolysis was performed in an H-type electrolytic cell with a Nafion®117 membrane as a separator. The three-electrode system includes a Ag/AgCl electrode, platinum foil (2 cm²), and glass carbon electrode (3 mm) as the reference, counter and working electrodes, respectively. Before electrolysis, CO₂ (99.995%) was bubbled in 0.1 M KHCO₃ electrolyte for 30 min. All potentials were converted to the reversible hydrogen electrode (RHE) on the basis of the Nernst equation:

$$E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.197 + 0.0591 \times \text{pH}$$

The total amount of CO produced was measured by gas

chromatography (SRI 8610C). A GC run was initiated every 30 min. High purity Ar (99.999%) was used as the carrier gas. The faradaic efficiencies of the gas products were calculated as follows:

$$FE = nFA\alpha v_i / j_{\text{total}}$$

where $n = 2$ is the number of electrons transferred per mole of CO, F is the Faraday constant, A is the integral area of the gas-phase products CO or H₂, α is the conversion factor determined from the calibration of the GC with standard samples, v_i is the flow rate of CO₂, and j_{total} is the total current at each applied potential.

2.5. Calculations

The density functional theory (DFT) calculations were performed using the VASP package of Perdew-Burke-Ernzerhof [51,52]. The structures were relaxed until the residual force on each atom was less than 0.01 eV Å⁻¹. The energy cutoff of plane wave functions was set to 500 eV. Moreover, 14 Å vacuum layers were used. The reciprocal space was sampled using a 3 × 3 × 1 point grid by the Monkhorst-Pack K-points scheme. A 10 × 10 × 1 graphene supercell was used. The adsorption energy was calculated according to the following formula:

$$E_a = E_{\text{final}} - E_{\text{substrate}} - E_{\text{adsorbate}}$$

where E_a is the adsorption energy of the adsorbed COOH* and CO*, E_{final} is the total energy of the adsorbed substance on the substrate, $E_{\text{substrate}}$ is the total energy of the substrate, and $E_{\text{adsorbate}}$ is the total energy of the adsorbate.

Based on the calculated hydrogen electrode (CHE) model, the free energy diagram was calculated at 0 V_{RHE}. The Gibbs free energy (ΔG) could be expressed as follows:

$$\Delta G = E_a + \Delta ZPE - T\Delta S$$

where ΔZPE and $T\Delta S$ are the zero-point energy correction and entropic energy, respectively.

3. Results and discussion

3.1. Physical characterization

N/S dual-doped high-surface-area hollow carbon nanospheres were synthesized by a facile approach, which is schematically depicted in Scheme 1. PACP-Zn was fabricated by the polymerization of aniline and pyrrole at the interface of Triton X-100 micelles in the presence of ZnCl₂ salt and hydrophilic oxidant APS [53]. ZnCl₂ diffused onto the PACP nanospheres at various positions, which had no discernible effect on polymeri-

Scheme 1. Schematic illustration of the synthesis process of SZ-HCN. (a) Polymerization of pyrrole and aniline; (b) Pyrolysis is synchronous with sulfuration at 900 °C.

zation. Moreover, the as-prepared PACP-Zn and S powder were placed in a porcelain boat for heat treatment at 900 °C for 2 h to yield the target N/S dual-doped product (SZ-HCN). Notably, ZnCl₂ salts were volatilized during calcination, leading to the formation of abundant pores, and in turn, a porous structure.

SEM and TEM images remarkably showed well-defined nanospheres of the samples (Figs. 1 and S1), which demonstrated that the total diameter of the nanospheres ranged from 70 to 120 nm. TEM images (Fig. 1(c) and 1(d)) display the hollow structure of SZ-HCN, having the inner diameter ranging from 40 to 60 nm. This hollow structure may provide high SSA and favorable channels for transportation and penetration of the electrolyte and related CO₂RR species. Comparison of reference catalysts (Figs. 1 and S2) confirms that ZnCl₂ salts serve as a sacrificial template and enable the formation of the nanoporous structure without destroying the hollow structure. In Figs. S2(a) and S2(b), the SEM and TEM images showed that the CN sample was a solid nanosphere without a hollow structure and different diameters, revealing that Triton X-100 as the micelle template assisted the formation of the hollow structure. The HAADF-STEM (Fig. 1(c)) and corresponding EDS images (Fig. 1(d)–(g)) of SZ-HCN revealed that N and S species were uniformly distribute on the carbon matrix, confirming the successful introduction of N and S atoms.

Fig. 2(a) shows the XRD patterns of the carbon samples, exhibiting two broad peaks at approximately $2\theta = 25^\circ$ and 44° . The peaks were characteristic of (002) and (101) planes (JCPDS no. 34-0567), demonstrating that the samples possessed a strong graphitic structure [54,55]. There were no diffraction peaks of crystalline Zn or Zn compounds. The Raman spectrum (Fig. 2(b)) indicated two distinctive peaks at 1340 and 1575 cm⁻¹, corresponding to the D and G bands, respectively. The D band was attributed to the defective/disordered carbon and G band to the graphitic *sp*²-carbon [56,57]. Nitrogen

Fig. 1. TEM images of (a, b) SZ-HCN. (c) HAADF image and (d–g) elemental mapping of SZ-HCN.

Fig. 2. (a) XRD patterns; (b) Raman spectrum; (c) N_2 adsorption isotherms; (d) Pore size distributions.

adsorption-desorption curves were categorized as type-IV isotherms with pronounced H4 hysteresis loops (Fig. 2(c)), revealing the existence of mesoporous and microporous structures. The BET specific surface areas were evaluated on the basis of the Brunauer-Emmett-Teller (BET) model. The specific surface areas of SZ-HCN ($1510 \text{ m}^2 \text{ g}^{-1}$) and Z-HCN ($1390 \text{ m}^2 \text{ g}^{-1}$) were remarkably higher than those of S-HCN ($815 \text{ m}^2 \text{ g}^{-1}$) and HCN ($790 \text{ m}^2 \text{ g}^{-1}$), which could be attributed to the addition of $ZnCl_2$ salts. Moreover, the pore size distribution curves (Fig. 2(d)) were evaluated in the range of 1–10 nm, exhibiting the coexistence of microporous and mesoporous structures. It is well known that highly porous structures could provide abundant three phase interfaces for convenient mass transport and accessibility of the related CO_2RR species [58].

The survey XPS spectra of SZ-HCN (Fig. 3(a)) showed the presence of C, O, N, and S, which is in agreement with EDS results. The high-resolution C 1s XPS spectrum of SZ-HCN (Fig. 3(b)) revealed different peaks including those for C=C (284.8 eV), C=N (285.4 eV), C–O (286.2 eV), C–N (287.1 eV), and C=O/O–C=O (289.1 eV) [59]. The N 1s spectrum (Fig. 3(c)) could be resolved into four peaks centered at 398.4, 399.6, 401.0, and 402.7 eV, which were assigned respectively to pyridinic-N, pyrrolic-N, graphitic-N, and oxidized nitrogen [60]. Figs. 3(a) and 3(b) suggested that N atoms were successfully doped. Notably, pyridinic-N with a negative charge as active sites has the potential to adsorb CO_2 molecules for facilitating CO_2RR [61–63]. The S 2p XPS spectrum (Fig. 3(d)) was deconvoluted into three peaks at 163.8, 165.1, and 168.5 eV, corre-

sponding to C–S ($2p_{3/2}$), C–S–C ($2p_{1/2}$) and C– SO_x –C, respectively. The success of dual doping can be attributed to the synergistic effect of S and N, which could enhance the CO_2RR activity because of the modification of the interactions between the C and S and N atoms [29,48,64].

3.2. Electrochemical measurements

To evaluate the electrochemical CO_2 reduction reaction activity, experiments using a three-electrode system were carried out in N_2 - and CO_2 -saturated 0.1 M $KHCO_3$ electrolyte. The CO_2RR activity of SZ-HCN was first evaluated based on linear sweep voltammetry (LSV) polarization curves (Fig. 4(a)). When the potential was swept in the range from 0 to -1.2 V versus RHE, only CO and H_2 were detected in the final products by an on-line gas chromatograph. SZ-HCN exhibited higher reductive currents under a CO_2 atmosphere than under a N_2 atmosphere, manifesting the suppressed HER activity on SZ-HCN by CO_2RR . Fig. 4(b) shows that SZ-HCN has the lowest onset potential of -0.40 V and the highest current density, indicating its highest CO_2RR activity among all samples. Quantification of the CO_2RR activity and selectivity was performed by the controlled-potential bulk electrolysis method. As seen in Fig. 4(c), the Faradaic efficiency (FE) for CO toward SZ-HCN gradually increased from -0.30 to -0.60 V and reached the maximum value (93%) at -0.60 V . Meanwhile, the competitive HER was suppressed with the FE of H_2 being than 10% (Fig. S4(a)). At low potentials, the CO FE of SZ-HCN decreased because the

Fig. 3. (a) Survey XPS spectra; high-resolution C 1s (b), N 1s (c) and S 2p (d) XPS spectra of SZ-HCN.

competitive HER was dominant. Additionally, SZ-HCN achieved the maximum CO FE (93%) among those for Z-HCN (84%), S-HCN (40%), and HCN (21%). Through a comparison of the CRR performance of Z-HCN and HCN, it was found that a high SSA and nanoporous structures formed by the volatilization of ZnCl_2 salts facilitate the exposure of more active sites and lead to enhanced activity for the CO_2RR . In Fig. S3, CN catalysts demonstrated a lower current density and a more negative onset potential than those of HCN, probably because the solid nanospheres without a hollow structure provided less three phase interfaces, which is inconvenient for mass transport and results in poor accessibility of the related CO_2RR species. In addition, electrochemical active surface area (ECSA) analysis was carried out based on electrochemical double-layer capacitance (C_{dl}) (Figs. S4(b) and S5) [65]. The C_{dl} values of SZ-HCN, Z-HCN, S-HCN, and HCN were calculated as 26.81, 24.55, 16.56, and 16.03 mF cm^{-2} , respectively. C_{dl} of Z-HCN was larger than that of HCN, also suggesting that Z-HCN had more exposed catalytic active sites for electrolysis during the CO_2RR . Although there was no significant difference in C_{dl} between SZ-HCN and Z-HCN, the CO_2RR performance of SZ-HCN was superior to that of Z-HCN, which demonstrated the dual doping of N and S atoms improved the activity of the active sites to a greater extent than that in the case of N doping alone. Tafel analysis was carried out to determine the kinetics of the CO_2RR on different catalysts. In Fig. 4(d), the measured Tafel slope of SZ-HCN (122 mV dec^{-1}) was close to 118 mV dec^{-1} , revealing that sin-

gle-electron transfer of CO_2 to form COOH^* was the rate-determining step [66]. In comparison, the Tafel slope for SZ-HCN was smaller than that of other catalysts, which demonstrated the favorable kinetics for the formation of CO. The stability of the CO_2RR was further investigated by long-time durability measurements. As illustrated in Fig. 4(e), SZ-HCN, Z-HCN, S-HCN, and HCN were acquired by the potentiostatic method at a constant voltage of -0.60 V for 20 h, which indicated their excellent durability. After each 2 h interval, the outlet gases were collected and analyzed by GC, and the corresponding CO FE was calculated. The SZ-HCN catalyst still presented a stable current density of -5.2 mA cm^{-2} , with a high CO FE for 20 h (Fig. 4(f)), which revealed its remarkable long-term stability during electrochemical operation.

3.3. DFT calculations

To further probe the impact of N and S dual doping on the mechanism underlying the CO_2 -to-CO reduction, DFT calculations were carried out. Based on previous studies, the electron-withdrawing nitrogen with a similar size as the C atom but larger electronegativity ($\chi = 3.04$) can be efficiently doped into carbon, which alters the charge polarization and asymmetrical electron spin density. The pyridinic nitrogen with a lone pair as a Lewis basic site has widely been considered as the active site for enhanced CO_2 adsorption, COOH^* formation, and CO^* desorption in CO_2 -to-CO reduction [61–63,67–69]. As per the

Fig. 4. (a) LSV curves of SZ-HCN in CO_2 -saturated and N_2 -saturated 0.1 M KHCO_3 solution; (b) LSV curves in CO_2 -saturated solution, in the presence of various electrocatalysts; (c) Faradaic efficiencies of CO by capitalizing on various cathodes at potentials ranging from -0.30 to -1.0 V versus RHE; (d) Tafel plots of different samples; (e) Chronoamperometric curves of stability test and (f) stability of faradaic efficiency for CO_2 reduction at -0.60 V in the CO_2 -saturated 0.1 M KHCO_3 solution.

periodic table of elements, S has a larger atomic size than C but similar electronegativity ($\chi = 2.58$ and 2.55 , respectively), which results in high spin densities within the surrounding C atoms [70]. S doping can modify the electronic interactions on the C atoms and thus enhance the catalytic activity [71]. We propose a possible reaction mechanism ($\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{CO} + \text{H}_2\text{O}$) involving two consecutive proton-electron coupling reactions and two intermediates (COOH^* and CO^*), as illustrated in Fig. 5(a) [72]. On the basis of the CO_2 -to-CO reaction pathway, the free energy diagram was calculated (Fig. 5(b)). Both SZ-HCN and Z-HCN had a large Gibbs free energy change (ΔG) for the formation of COOH^* , which revealed that the first

proton-coupled electron transfer was the rate-determining step. The calculation results in Fig. 5(b) show that ΔG for COOH^* adsorption on the pyridinic N adjacent to the C-bonded S was lower than that for the pure pyridinic N, indicating that Z-HCN must overcome a higher reaction energy barrier to form COOH^* . This result was also in agreement with the results of Tafel analysis and the CO_2 RR activities of SZ-HCN and Z-HCN. Controlled experiments and theoretical results led us to conclude that the dual doping of N and S could improve the CO_2 RR performance. The difference between SZ-HCN and Z-HCN was ascribed to the additional incorporation of S, which induced a significant electron spin density redistribution.

Fig. 5. (a) Proposed mechanism for the nitrogen-doped catalytic site. (b) Calculated free energy diagram of CO_2 reduction to CO on N-doped Z-HCN and N,S dual-doped gSZ-HCN.

4. Conclusions

In summary, we have prepared N/S dual-doped hollow carbon materials by a simple micelle template-induced method and pyrolysis. Hollow and porous structures with a high SSA not only offered adequate electrolyte/electrode contact area but also provided abundant channels for faster transportation of the CO₂RR-related species. DFT calculations revealed that the additional S doping could offer more active sites, thus decreasing the ΔG value for the formation of the COOH* intermediate toward the electrocatalytic reduction of CO₂ to CO. The SZ-HCN catalyst showed high activity and selectivity for CO₂-to-CO reduction along with good long-term stability; the CO Faradaic efficiency was as high as ~93% at a low potential of –0.60 V. Our work provides a robust porous carbon electrocatalyst with heteroatom doping for efficient and selective CO₂ reduction, which has the potential to replace expensive noble metal catalysts.

References

- [1] P. De Luna, C. Hahn, D. Higgins, S. A. Jaffer, T. F. Jaramillo, E. H. Sargent, *Science*, **2019**, 364, eaav3506.
- [2] J. Hao, W. Shi, *Chin. J. Catal.*, **2018**, 39, 1157–1166.
- [3] Y. F. Wang, P. Han, X. M. Lv, L. J. Zhang, G. F. Zheng, *Joule*, **2018**, 2, 2551–2582.
- [4] Z. Gu, H. Shen, L. Shang, X. Lv, L. Qian, G. Zheng, *Small Methods*, **2018**, 2, 1800121.
- [5] C. Yan, L. Lin, G. Wang, X. Bao, *Chin. J. Catal.*, **2019**, 40, 23–37.
- [6] Z. Sun, T. Ma, H. Tao, Q. Fan, B. Han, *Chem*, **2017**, 3, 560–587.
- [7] E. R. Cave, C. Shi, K. P. Kuhl, T. Hatsukade, D. N. Abram, C. Hahn, K. Chan, T. F. Jaramillo, *ACS Catal.*, **2018**, 8, 3035–3040.
- [8] J. Rosen, G. S. Hutchings, Q. Lu, S. Rivera, Y. Zhou, D. G. Vlachos, F. Jiao, *ACS Catal.*, **2015**, 5, 4293–4299.
- [9] S. Narayanaru, J. Chinnaiiah, K. L. Phani, F. Scholz, *Electrochim. Acta*, **2018**, 264, 269–274.
- [10] W. Zhu, L. Zhang, P. Yang, C. Hu, Z. Luo, X. Chang, Z. J. Zhao, J. Gong, *Angew. Chem. Int. Ed.*, **2018**, 57, 11544–11548.
- [11] H. P. Yang, Q. Lin, H. W. Zhang, G. D. Li, L. D. Fan, X. Y. Chai, Q. L. Zhang, J. H. Liu, C. X. He, *Chem. Commun.*, **2018**, 54, 4108–4111.
- [12] W. Zhan, J. Wang, H. Wang, J. Zhang, X. Liu, P. Zhang, M. Chi, Y. Guo, Y. Guo, G. Lu, S. Sun, S. Dai, H. Zhu, *J. Am. Chem. Soc.*, **2017**, 139, 8846–8854.
- [13] X. Bai, W. Chen, C. Zhao, S. Li, Y. Song, R. Ge, W. Wei, Y. Sun, *Angew. Chem. Int. Ed.*, **2017**, 56, 12219–12223.
- [14] M. Ma, H. A. Hansen, M. Valenti, Z. Wang, A. Cao, M. Dong, W. A. Smith, *Nano Energy*, **2017**, 42, 51–57.
- [15] Z. Chen, K. Mou, X. Wang, L. Liu, *Angew. Chem. Int. Ed.*, **2018**, 57, 12790–12794.
- [16] Y. Yilguma, Z. Wang, C. Yang, A. Guan, L. Shang, A. M. Al-Enizi, L. Zhang, G. Zheng, *J. Mater. Chem. A*, **2018**, 6, 20121–20127.
- [17] L. Liu, N. Tian, L. Huang, Y.-H. Hong, A.-Y. Xie, F.-Y. Zhang, C. Xiao, Z.-Y. Zhou, S.-G. Sun, *Chin. J. Catal.*, **2016**, 37, 1070–1075.
- [18] P. Kang, C. Cheng, Z. Chen, C. K. Schauer, T. J. Meyer, M. Brookhart, *J. Am. Chem. Soc.*, **2012**, 134, 5500–5503.
- [19] Z. Cao, J. S. Derrick, J. Xu, R. Gao, M. Gong, E. M. Nichols, P. T. Smith, X. Liu, X. Wen, C. Coperet, C. J. Chang, *Angew. Chem. Int. Ed.*, **2018**, 57, 4981–4985.
- [20] B. M. Szyja, *ChemElectroChem*, **2018**, 5, 2105–2112.
- [21] G. Yang, Z. Yu, J. Zhang, Z. Liang, *Chin. J. Catal.*, **2018**, 39, 914–919.
- [22] Y. Zhou, F. Che, M. Liu, C. Zou, Z. Liang, P. De Luna, H. Yuan, J. Li, Z. Wang, H. Xie, H. Li, P. Chen, E. Bladt, R. Quintero-Bermudez, T.-K. Sham, S. Bals, J. Hofkens, D. Sinton, G. Chen, E. H. Sargent, *Nat. Chem.*, **2018**, 10, 974–980.
- [23] Q. Lu, F. Jiao, *Nano Energy*, **2016**, 29, 439–456.
- [24] D. J. Wilhelm, D. R. Simbeck, A.D. Karp, R. L. Dickenson, *Fuel Pro-*

Graphical Abstract

Chin. J. Catal., 2020, 41: 830–838 doi: S1872-2067(19)63485-6

Nitrogen and sulfur dual-doped high-surface-area hollow carbon nanospheres for efficient CO₂ reduction

Guodong Li, Yongjie Qin, Yu Wu, Lei Pei, Qi Hu, Hengpan Yang, Qianling Zhang, Jianhong Liu, Chuanxin He*
University of Science and Technology of China; Shenzhen University

A N and S dual-doped carbon-based catalyst with a high specific surface area was prepared via a facile route, which showed remarkably high activity and selectivity for CO₂-to-CO electroreduction, along with excellent stability.

- cess. *Technol.*, **2001**, 7, 139–148.
- [25] Q. Lu, J. Rosen, Y. Zhou, G. S. Hutchings, Y. C. Kimmel, J. G. Chen, F. Jiao, *Nat. Commun.*, **2014**, 5, 3242.
- [26] W. Zhu, Y. J. Zhang, H. Zhang, H. Lv, Q. Li, R. Michalsky, A. A. Peterson, S. Sun, *J. Am. Chem. Soc.*, **2014**, 136, 16132–16135.
- [27] R.-H. Guo, C.-F. Liu, T.-C. Wei, C.-C. Hu, *Electrochem. Commun.*, **2017**, 80, 24–28.
- [28] Y. S. Ham, S. Choe, M. J. Kim, T. Lim, S.-K. Kim, J. J. Kim, *Appl. Catal. B*, **2017**, 208, 35–43.
- [29] X. Duan, J. Xu, Z. Wei, J. Ma, S. Guo, S. Wang, H. Liu, S. Dou, *Adv. Mater.*, **2017**, 29, 1701784.
- [30] J. Xie, X. Zhao, M. Wu, Q. Li, Y. Wang, J. Yao, *Angew. Chem. Int. Ed.*, **2018**, 57, 9640–9644.
- [31] M. A. Ghausi, J. Xie, Q. Li, X. Wang, R. Yang, M. Wu, Y. Wang, L. Dai, *Angew. Chem. Int. Ed.*, **2018**, 57, 13135–13139.
- [32] J. Wu, R. M. Yadav, M. Liu, P. P. Sharma, C. S. Tiwary, L. Ma, X. Zou, X. D. Zhou, B. I. Yakobson, J. Lou, P. M. Ajayan, *ACS Nano*, **2015**, 9, 5364–5371.
- [33] Y. Liu, S. Chen, X. Quan, H. Yu, *J. Am. Chem. Soc.*, **2015**, 137, 11631–11636.
- [34] Y. Zhao, J. J. Liang, C. Y. Wang, J. M. Ma, G. G. Wallace, *Adv. Energy Mater.*, **2018**, 8, 1702524.
- [35] P. Han, X. Yu, D. Yuan, M. Kuang, Y. Wang, A. M. Al-Enizi, G. Zheng, *J. Colloid Interface Sci.*, **2019**, 534, 332–337.
- [36] Y. Song, W. Chen, C. Zhao, S. Li, W. Wei, Y. Sun, *Angew. Chem. Int. Ed.*, **2017**, 56, 10840–10844.
- [37] X. Sun, L. Lu, Q. Zhu, C. Wu, D. Yang, C. Chen, B. Han, *Angew. Chem. Int. Ed.*, **2018**, 57, 2427–2431.
- [38] F. Li, M. Xue, G. P. Knowles, L. Chen, D. R. MacFarlane, J. Zhang, *Electrochim. Acta*, **2017**, 245, 561–568.
- [39] H. Wang, J. Jia, P. Song, Q. Wang, D. Li, S. Min, C. Qian, L. Wang, Y. F. Li, C. Ma, T. Wu, J. Yuan, M. Antonietti, G. A. Ozin, *Angew. Chem. Int. Ed.*, **2017**, 56, 7847–7852.
- [40] N. P. Wickramaratne, J. Xu, M. Wang, L. Zhu, L. Dai, M. Jaroniec, *Chem. Mater.*, **2014**, 26, 2820–2828.
- [41] Y. Pan, R. Lin, Y. Chen, S. Liu, W. Zhu, X. Cao, W. Chen, K. Wu, W. C. Cheong, Y. Wang, L. Zheng, J. Luo, Y. Lin, Y. Liu, C. Liu, J. Li, Q. Lu, X. Chen, D. Wang, Q. Peng, C. Chen, Y. Li, *J. Am. Chem. Soc.*, **2018**, 140, 4218–4221.
- [42] A. Kong, X. Zhu, Z. Han, Y. Yu, Y. Zhang, B. Dong, Y. Shan, *ACS Catal.*, **2014**, 4, 1793–1800.
- [43] Y. Chang, F. Hong, J. Liu, M. Xie, Q. Zhang, C. He, H. Niu, J. Liu, *Carbon*, **2015**, 87, 424–433.
- [44] G. A. Ferrero, K. Preuss, A. Marinovic, A. B. Jorge, N. Mansor, D. J. Brett, A. B. Fuentetaja, M. Sevilla, M. M. Titirici, *ACS Nano*, **2016**, 10, 5922–5932.
- [45] J. Liang, Y. Jiao, M. Jaroniec, S. Z. Qiao, *Angew. Chem. Int. Ed.*, **2012**, 51, 11496–11500.
- [46] R. Li, Z. Wei, X. Gou, *ACS Catal.*, **2015**, 5, 4133–4142.
- [47] J. Wang, J. Hao, D. Liu, S. Qin, D. Portehault, Y. Li, Y. Chen, W. Lei, *ACS Energy Lett.*, **2017**, 2, 306–312.
- [48] H. Yang, Y. Wu, Q. Lin, L. Fan, X. Chai, Q. Zhang, J. Liu, C. He, Z. Lin, *Angew. Chem. Int. Ed.*, **2018**, 57, 15476–15480.
- [49] G. Li, L. Pei, Y. Wu, B. Zhu, Q. Hu, H. Yang, Q. Zhang, J. Liu, C. He, *J. Mater. Chem. A*, **2019**, 7, 11223–11233.
- [50] G. Han, Y. H. Jin, R. A. Burgess, N. E. Dickenson, X. M. Cao, Y. Sun, *J. Am. Chem. Soc.*, **2017**, 139, 15584–15587.
- [51] J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, C. Fiolhais, *Phys. Rev. B*, **1992**, 46, 6671–6687.
- [52] G. Kresse, J. Furthmüller, *Comp. Mater. Sci.*, **1996**, 6, 15–50.
- [53] C. Zhou, J. Han, G. Song, R. Guo, *J. Polym. Sci., Part A*, **2008**, 46, 3563–3572.
- [54] Y. Li, H. Zhang, Y. Wang, P. Liu, H. Yang, X. Yao, D. Wang, Z. Tang, H. Zhao, *Energy Environ. Sci.*, **2014**, 7, 3720–3726.
- [55] J. Li, Y. J. Song, G. X. Zhang, H. Y. Liu, Y. R. Wang, S. H. Sun, X. W. Guo, *Adv. Funct. Mater.*, **2017**, 27, 1604356.
- [56] F. Tuinstra, J. L. Koenig, *J. Chem. Phys.*, **1970**, 53, 1126.
- [57] R. J. Nemanich, S. A. Solin, *Phys. Rev. B*, **1979**, 20, 392–401.
- [58] C. Tang, H. F. Wang, Q. Zhang, *Acc. Chem. Res.*, **2018**, 51, 881–889.
- [59] J. Yang, H. Sun, H. Liang, H. Ji, L. Song, C. Gao, H. Xu, *Adv. Mater.*, **2016**, 28, 4606–4613.
- [60] Y. Zhao, R. Nakamura, K. Kamiya, S. Nakanishi, K. Hashimoto, *Nat. Commun.*, **2013**, 4, 2390.
- [61] P. P. Sharma, J. Wu, R. M. Yadav, M. Liu, C. J. Wright, C. S. Tiwary, B. I. Yakobson, J. Lou, P. M. Ajayan, X. D. Zhou, *Angew. Chem. Int. Ed.*, **2015**, 54, 13701–13705.
- [62] J. Wu, M. Liu, P. P. Sharma, R. M. Yadav, L. Ma, Y. Yang, X. Zou, X. D. Zhou, R. Vajtai, B. I. Yakobson, J. Lou, P. M. Ajayan, *Nano Lett.*, **2016**, 16, 466–470.
- [63] S. Liu, H. B. Yang, X. Huang, L. H. Liu, W. Z. Cai, J. J. Gao, X. N. Li, T. Zhang, Y. Q. Huang, B. Liu, *Adv. Funct. Mater.*, **2018**, 28, 1800499.
- [64] W. Li, M. Seredych, E. Rodriguez-Castellon, T. J. Bandoz, *ChemSusChem*, **2016**, 9, 606–616.
- [65] H. P. Yang, H. W. Zhang, Y. Wu, L. D. Fan, X. Y. Chai, Q. L. Zhang, J. H. Liu, C. X. He, *ChemSusChem*, **2018**, 11, 3905–3910.
- [66] K. Jiang, S. Siahrostami, T. Zheng, Y. Hu, S. Hwang, E. Stavitski, Y. Peng, J. Dynes, M. Gangisetty, D. Su, K. Attenkofer, H. Wang, *Energy Environ. Sci.*, **2018**, 11, 893–903.
- [67] P. Jiang, J. Chen, C. Wang, K. Yang, S. Gong, S. Liu, Z. Lin, M. Li, G. Xia, Y. Yang, J. Su, Q. Chen, *Adv. Mater.*, **2018**, 30, 1705324.
- [68] H. Kiuchi, R. Shibuya, T. Kondo, J. Nakamura, H. Niwa, J. Miyawaki, M. Kawai, M. Oshima, Y. Harada, *Nanoscale Res. Lett.*, **2016**, 11, 127.
- [69] J. Wei, D. Zhou, Z. Sun, Y. Deng, Y. Xia, D. Zhao, *Adv. Funct. Mater.*, **2013**, 23, 2322–2328.
- [70] K. Gao, B. Wang, L. Tao, B. V. Cunnings, Z. Zhang, S. Wang, R. S. Ruoff, L. Qu, *Adv. Mater.*, **2019**, 31, e1805121.
- [71] J. Wu, T. Sharifi, Y. Gao, T. Zhang, P. M. Ajayan, *Adv. Mater.*, **2019**, 31, e1804257.
- [72] R. Kortlever, J. Shen, K. J. Schouten, F. Calle-Vallejo, M. T. Koper, *J. Phys. Chem. Lett.*, **2015**, 6, 4073–4082.

氮硫共掺杂高比表面中空碳球的制备及其在电催化二氧化碳还原中的应用

李国栋^{a,b}, 覃永杰^b, 吴玉^{a,b}, 裴蕾^b, 胡琪^b, 杨恒攀^b, 张黔玲^b, 刘剑洪^b, 何传新^{b,*}

^a中国科学技术大学化学物理系, 安徽合肥230026

^b深圳大学化学与环境工程学院, 广东深圳518060

摘要: 化石燃料是现代能源体系的重要支柱, 其大量使用导致大气中CO₂浓度不断增加, 加剧了全球变暖和环境恶化。因此, 各国研究人员开发了大量技术手段以捕获和重新再利用CO₂这一丰富的碳资源。其中, CO₂电催化还原(CO₂RR)技术在

减少CO₂排放和将其转化为有用化学品等方面极具潜力。但是, CO₂RR具有反应能垒高和动力学过程缓慢等特点, 进而限制其转化效率, 故使用传统的贵金属材料(Ag, Au, Cu及Pd等)作为CO₂RR高效的催化剂。然而, 贵金属材料的大规模应用受限于它们成本高昂、稳定性差及环境毒性等缺点。在各类可替代贵金属催化剂中, 碳材料因其廉价丰富、结构可调 and 导电性高的特点在CO₂RR应用上展现出诱人的前景, 因此, 探索合适的碳基催化剂在高效催化二氧化碳领域具有重要的研究价值和意义。

本文通过简单有效的方法制备了一种氮硫共掺杂的高比表面的碳基催化剂(SZ-HCN)用于CO₂RR。首先利用表面活性剂胶束Triton X-100作为模板诱导调控, 合成了具有中空结构的苯胺-吡咯共聚物, 并以此为碳前驱体, 通过一步热解共聚物和硫粉获得N和S共掺杂多孔碳, 材料的高比表面积(1510 m² g⁻¹)得益于中空结构和ZnCl₂盐造成的纳米孔结构。值得注意的是, 高比表面的多孔结构且有效共掺杂N/S, 能提供更多的高活性催化位点和有利于相关反应物种的传输。通过扫描电子显微镜、高分辨透射电子显微镜、高角环形暗场-扫描透射-元素分布、N₂吸脱附等温分析及X射线光电子能谱等物理表征证实了催化剂材料的中孔结构和N/S共掺杂组分。进一步通过电化学测试分析和产物测试分析可知, 电催化剂SZ-HCN在-0.60 V还原CO₂为CO的法拉第效率高达93%, 明显抑制竞争反应HER。此外, 在-0.60 V恒电位下连续20 h测试, 依旧保持稳定的电流密度(-5.2 mA cm⁻²)和高的CO选择性, 显示了出色的耐久性和潜在应用性。

我们采用密度泛函理论探究N和S掺杂的影响, 模拟计算可知, 相比单一N掺杂的催化剂, N, S共掺杂可以提供更多的活性位点, 降低CO₂还原为CO反应中决速步生成COOH*的吉布斯自由能垒, 进而提高催化活性。SZ-HCN催化剂展现出的优异CO₂RR活性和稳定性主要归因于: (1) N和S元素均匀掺杂到碳基体中, 两者的协同效应导致碳电荷再分布形成高活性位点, 提高本征活性; (2)高比表面的多级孔结构提供了丰富的三相接触界面和有利的传输通道, 便于反应相关物种的快速转移。该碳基催化剂材料在替代贵金属应用于CO₂RR展示了一定的潜力。

关键词: 高比表面; 中空结构; 碳基催化剂; CO₂电还原; 电催化选择性

收稿日期: 2019-09-25. 接受日期: 2019-10-29. 出版日期: 2020-05-05.

*通讯联系人. 电话: (0755)26534173; 传真: (0755)26536141; 电子信箱: hecx@szu.edu.cn

基金来源: 国家自然科学基金(21574084, 21571131); 广东省自然科学基金(2017A040405066); 深圳市科技计划项目(JCYJ20160308104704791, JCYJ20170818091657056).

本文的电子版全文由Elsevier出版社在ScienceDirect上出版(<http://www.sciencedirect.com/science/journal/18722067>).