Pd-based catalysts with preferred morphologies and compositions are of great significance for boosting oxygen reduction reaction (ORR) and formic acid oxidation reaction (FAOR) performance, but the development of facile preparation methods is challenging. Therefore, an unconventional strategy is proposed to synthesize palladium-copper cyanogel (Cu₄-Pd(CN)₄)₂·6H₂O and subsequently induce the formation of PdCu alloy nanocorals (ANCs), which has the advantages of being simple, green, and efficient. The synthesized PdCu ANCs consist of a 3D porous network structure and Pd-enriched surface, which is beneficial to exposing more accessible active sites, accelerating mass/electron transfer rate, and strengthening chemical stability. By virtue of these merits, the PdCu ANCs exhibit superior activity and stability in both FAOR and ORR. Remarkably, the mass activity of PdCu ANCs catalyst in FAOR reaches 554.53 mA mg⁻¹, with a 4.8-fold enhancement compared to commercial Pd black. And the half-wave potential of 0.861 V of PdCu ANCs catalyst in ORR surpasses the values of commercial Pd black and Pt black catalysts.

1. Introduction

Direct formic acid fuel cell (DFAFC) is a promising electrochemical energy conversion device, which possesses integrated merits, including high power densities (1740 Wh kg⁻¹), nontoxicity, low permeability and easy storage, sealing and transport. Nevertheless, the major limitation to further commercialization of DFAFC remains the sluggish reaction kinetics of cathodic oxygen reduction reactions (ORR) and anodic formic acid oxidation reaction (FAOR). Palladium (Pd), as an alternative material of Pt, has been widely used in ORR because of its comparable performance. Moreover, the direct dehydrogenation pathway is more profitable on Pd than on Pt in FAOR, which is manifested by faster reaction kinetics, lower oxidation potential, better anti-CO poisoning, and higher selectivity catalytic activity. In spite of that, Pd has still suffered from difficulty in electrocatalytic property and soaring prices.

Alloying Pd with cheap transition metals (Co, Fe, Ni, and Cu) is an effective strategy to increase its catalytic performance and utilization efficiency. Among them, Cu plays a great promoting role in the catalytic performance of PdCu alloy by changing the electronic structure and modulating the d-band centre of Pd, and creating physicochemical synergies. Zhang et al. reported that the peak current density of synthesized web-footed PdCu nanosheets is 3.0 and 7.4 times higher than that of Pd nanosheets and commercial Pd/C catalyst in FAOR, respectively, indicating that the introduction of Cu could adjust the electronic structure of Pd and reduce CO poisoning. Furthermore, Henkelman et al. investigated the activity of PdCu random alloy catalyst in ORR. The results disclosed that the charge transfer between Cu and Pd reduces the d-band of Pd, thus decreasing the oxygen binding energy of Pd, which is beneficial to improving the activity of PdCu in ORR. Apart from component regulation to improve the intrinsic activity, tailoring the desirable morphology to increase the number of active sites of catalysts can achieve another effective approach for advanced electrocatalytic performance. At present, a variety of Pd-based catalysts with unique morphology have been constructed, including 0D geometric nanoparticles, 1D nanorods and nanowires, 2D nanosheets and 3D networked nanostructures. In particular, the 3D structure often can endow superior electrocatalytic performance of the Pd-based catalysts via maximizing the exposed active area, creating high active sites available, and maintaining extremely suitable nanostructure. Moreover, 3D porous structure can facilitate mass/electron transfer between catalyst surface and substrate molecules, which is substantial for boosting the reaction kinetics and ultimate electrocatalytic properties. Although the methods these advantages, the
methods to synthesize 3D nanostructures are often complicated, commonly requiring two or more steps. Therefore, it is meaningful to synthesize 3D nanostructured PdCu alloy catalysts by a simple and highly effective method.

Cyanogel, formed by the repeated coordination of metal ion and cyanogroup (M-CN-M’, M = Fe, Co, Ni, Pd, Pt), can be used as ideal precursors for noble metal-based alloy catalysts with 3D structures. Cyanogel reduction has several unique merits: i) The preparation process is simple and the gelling conditions are not limited by air humidity, temperature and pressure for catalysts. ii) Uniform distribution of metal ions at the atomic scale in cyanogel facilitates the formation of alloy phases. iii) Characteristic 3D backbone of cyanogel can be effectively transformed into 3D porous structure of catalyst. Moreover, NaBH₄, as a strong reducing agent, can rapidly reduce Pd and Cu ions to achieve the formation of PdCu alloy. At present, the reported Pd-based cyanogels include Pd₃[Ni(CN)₄]·aH₂O, Pd₃[Fe(CN)₆]·aH₂O, and Pd₃[Co(CN)₆]·aH₂O, which are used to synthesize PdNi, PdFe and PdCo alloy, respectively, but there is no concern about PdCu cyanogel. The lack of research on PdCu cyanogel may be largely attributed to the instability of K₂Cu(CN)₄, which easily decomposes to copper (I) cyanide and releases toxic cyanide gas at room temperature. During this synthesis, the rapid polymerization of cyanogel was in situ formed into black PdCu ANCs by simple chemical reduction using freshly-prepared NaBH₄ solution at room temperature. Then, the as-synthesized bi-component Cuₓ[Pd(CN)₄]y·aH₂O cyanogel was in situ formed into black PdCu ANCs by simple chemical reduction using freshly-prepared NaBH₄ solution at room temperature. During this synthesis, the rapid polymerization of K₂Pd(CN)₄ and CuCl₂ occurs to form Pd-Cu-CN bonds by replacing chlorine ligand with cyanogroup, which provides a strong force to maintain the stability of 3D network structures. The uniform distribution of different metal ions in the 3D framework facilitates the formation of atomically dispersed alloys, thereby improving the alloying degree of catalyst. To further clarify the conditions for gelation, the feeding ratio of K₂Pd(CN)₄ and CuCl₂ were explored for control experiments (Figure S1, Supporting Information). The experimental results show that the cyanogel is not easy to form when the feed ratio is too low or too high compared to the standard condition, which may be the fact that excessive Cu ions cannot coordinate and too few Cu ions are not enough to form complete 3D skeleton.

The crystal structure of the prepared Cuₓ[Pd(CN)₄]y·aH₂O cyanogel was characterized by X-ray diffraction (XRD) pattern (Figure 1a). The result shows the amorphous peak shape of the classical Prussian-like structure, which corresponds to the peak positions of other Pd-based Prussian-like structures reported in the literature. Moreover, a set of peaks located at 24.55°, 28.41°, 58.80°, 64.67° and 73.92° belongs to standard KCl (JCPDS 72-1540), indicating the presence of by-product KCl rather than KCN during the cyanogel formation and the coordination between K₂Pd(CN)₄ and CuCl₂. The coordination was further verified by Fourier transform infrared (FT-IR) spectra. As shown in Figure 1b, there are distinct CN characteristic vibration peaks at 2192 and 538 cm⁻¹, respectively, and a Pd–C stretching vibration peak at 450 cm⁻¹, indicating the formation of Pd–C–Cu bonds. A sharp peak appeared at 1608 cm⁻¹, and a broad peak appeared between 3230 and 3580 cm⁻¹, which are attributed to the hydroxyl vibration peak of water, demonstrating that the obtained cyanogel contained crystal water. 3D structure of the cyanogel skeleton was confirmed by transmission electron microscope (TEM) and scanning TEM (STEM) image (Figure 1c,d), with the presence of grooves and pores on the surface. Energy-dispersive spectroscopy (EDS) spectrum (Figure S2a, Supporting Information) and element mapping images (Figure 1e) verify the homogeneous distribution of Pd, Cu and N in the cyanogel, demonstrating that Pd and Cu elements are cross-linked together in the cyanogel skeleton. In the secondary mass spectra (Figure S2b, Supporting Information), the main fragments can be observed as 927.3, 1001.3, 1076.3, and 1151.3, corresponding to Cu: Pd = 5:3, 6:3, 7:3, and 8:3, respectively, revealing that the coordination mode is not a single component.
phase, rather a diversity. X-ray photoelectron spectroscopy (XPS) spectra (Figure S3a,b, Supporting Information) of the cyanogel verify the presence of Pd and Cu in ionic state, consistent with the results of the FT-IR spectra.

Throughout chemical reduction using NaBH₄, 3D-structured PdCu ANCs were obtained. As identified by the XRD pattern (Figure 2a), the 2θ diffraction peaks appeared at 42.95°, 49.90°, 73.60°, and 89.47° are attributed to the (111), (200), (220), and (311) reflections of the face-centred cubic (fcc) Pd, respectively, and are in the standard between Pd (JCPDS 46-1043) and Cu (JCPDS 85-1326), indicating the formation of a PdCu alloy. For closed observation, it is found that there is a broad bulge on the left side of the PdCu alloy peak, which corresponds to the fcc Pd peak, indicating the possible existence of a Pd-enriched surface in PdCu ANCs catalyst. In Figure S4, Supporting Information, the EDS spectrum shows that the atomic contents of Pd and Cu in the PdCu ANCs is about 31.7% and 68.4%, respectively, which are consistent with the inductively coupled plasma mass spectrometry (ICP-MS) test results (atomic ratio: Pd/Cu = 31.8/68.2) and the feeding ratio. In general, the electrocatalytic reactions take place on the surface of catalysts, which means that the surface composition greatly affects the electrocatalytic performance. The molar ratio of Pd/Cu of surface composition of PdCu ANCs determined by XPS is 42.2/57.8, which is much higher than those of EDS and ICP, respectively, demonstrating Pd atoms are enriched on the surface of PdCu ANCs. Furthermore, Figure 2b discloses the modulation effect of Cu on the electronic structure of the Pd surface. The Pd 3d spectra of PdCu ANCs show the negative shift of 0.18 eV to lower binding energy compared to that of pure Pd probably owing to electron donation from Cu to Pd. The decrease in binding energy suggests that the d-band centre of Pd may shift downward, which conducive to weaken the interaction between the Pd surface and absorbates, thereby enhancing the catalytic activity.²⁵ The definite peaks at 335.0 and 340.3 eV for Pd 3d₅/₂ and Pd 3d₃/₂ of PdCu ANCs are featured, thus proving that the Pd species are metallic Pd⁰.⁶⁶ High-resolution XPS spectra of Cu 2p indicate the valence states of Cu ions in the Cu 2p₃/₂ and
Cu $2p_{1/2}$ orbitals (Figure 2c). The results confirm the formation of metallic Cu$^0$ and Cu$^{2+}$ within PdCu ANCs, which originate from partial oxidation of the surface exposed to air.$^{[61,62]}$ The high-resolution N 1s spectrum (Figure 2d) could be deconvoluted into two peaks located at 399.0 and 398.1 eV, which are assigned to pyrrolic N and pyridinic N, respectively, which may be due to the modification of a small amount of cyanogroup on the surface of the catalyst.

After simple chemical reduction, the obtained PdCu ANCs generally retain the hierarchically 3D and porous structure, as confirmed by scanning electron microscope (SEM) image (Figure 3a). The enlarged SEM images (Figure 3b) reveal that the coral-like nanostructure consists of continuous nanonetworks and abundant pores, which would endow catalyst with larger specific surface area, more active sites, and faster mass/electron transfer rates along the 3D framework. From the N$_2$ adsorption–desorption isotherms (Figure 3c), the surface area of PdCu ANCs catalyst was calculated to be 174.96 m$^2$ g$^{-1}$ by Brunauer–Emmett–Teller (BET). And the porous structure of PdCu ANCs with a pore diameter of about 3.3 nm was confirmed by pore-size distribution plot (inset in Figure 3c). In Figure 3d, the clear lattices can be captured by magnification, demonstrating the well-formed crystallinity of the PdCu ANCs. The lattice distance of PdCu ANCs measured by the high-resolution TEM (HRTEM) is 0.217 nm, which is between 0.229 nm of Pd (111) and 0.209 nm of Cu (111), further indicating that the obtained catalyst is PdCu alloy with Pd-enriched surface. Moreover, enlarged HRTEM image (Figure S5, Supporting Information) shows the presence of crystal steps and lattice defects on the surface of PdCu ANCs, which can increase the number of active sites and facilitate electron transport, thus improving electrocatalytic performance.$^{[63]}$ The successful fabrication of 3D porous network structure was also disclosed by high-angle annular dark-field scanning TEM (HAADF-STEM) images (Figure S6, Supporting Information). EDS line scanning (Figure 3f) and elemental mapping analysis (Figure 3g) show that Pd and Cu elements are distributed in the whole catalyst, which proves the existence of PdCu alloy. Further observation of mapping image shows that the signal intensity of Pd on the surface is stronger than that in the middle position, indicating that the catalysts are alloy phase with Pd-enriched surface, which may be attributed to the displacement reactions on the catalyst surface (Pd$^{2+}$ + Cu = Pd + Cu$^{2+}$). The Pd-enriched surface is beneficial to improve the utilization of Pd and the electrocatalytic performance.$^{[64,65]}$

Based on the unique structure and composition, the FAOR and ORR electrocatalytic performance of PdCu ANCs were evaluated, and commercial Pd black and Pt black were used as controls in a three-electrode system. Firstly, the typical cyclic voltammograms (CV) curves of the as-prepared PdCu ANCs and commercial Pd black were displayed in N$_2$-saturated 0.5 M H$_2$SO$_4$ solution at a sweep rate of 50 mV s$^{-1}$ (Figure 4a). Based on the reduction peak charge of CV, the electrochemical active surface areas (ECSA) of PdCu ANCs and Pd black were calculated to be 17.14 and 4.85 m$^2$ g$^{-1}$, respectively. The reduction peak potential on PdCu ANCs is negatively shifted by 47 mV compared to that of Pd black catalysts, indicating that PdCu ANCs can afford –OH species at a lower potential, which is favourable for the direct electron transfer pathway of FAOR.
Figure 4b and S7, Supporting Information, shows the CV curves of PdCu ANCs and Pd black catalysts in 0.5 M H2SO4 + 0.5 M HCOOH electrolyte, respectively. Compared with that of Pd black (113.42 mA mgPd−1, 2.29 mA cm−2) and reported Pd-based electrocatalysts (Table S1, Supporting Information), the PdCu ANCs exhibit higher mass activity (554.53 mA mgPd−1) and specific activity (3.24 mA cm−2), as well as a positive shift of 113.6 mV of onset potential for FAOR. From the Tafel plots in Figure 4c, the PdCu ANCs present a higher output current density than Pd black at the same polarization overpotential, suggesting favourable charge transfer and promoted reaction kinetics of FAOR. The turnover frequency (TOF), that is, the number of HCOOH molecules converted per activated Pd atom per second, is calculated according to the following formula: 

\[
\text{TOF} = \frac{j_k}{n_e N_s}, \quad \text{where } j_k, n, e, \text{ and } N_s \text{ are the specific peak current density of FAOR, } j_k \text{ the electron transfer number, elementary electric charge and the atomic density of the surface, respectively.}
\]

As indicated in Figure 4d, the PdCu ANCs represent more TOF (1.56) than commercial Pd black (1.10), indicating the high reactivity of PdCu ANCs to FAOR. This also indicates that the Pd atoms of the PdCu ANCs surface have a higher utilization rate, thus they can provide more catalytic active sites. The CO tolerance of PdCu ANCs and Pd black were evaluated via the CO-stripping voltammetry measurements shown in Figure 4e. The onset potential and peak potential of CO oxidation at PdCu ANCs shift negatively =169 and 118 mV, respectively, with respect to those on Pd black, manifesting that PdCu ANCs possess better COads intermediate tolerance capability toward the FAOR. Stability testing is a key indicator of FAOR performance.67 The chronoamperometric measurements were carried out in 0.5 M H2SO4 + 0.5 M HCOOH electrolyte at a constant potential of 0.44 V (Figure S8, Supporting Information). After 5,000 s, commercial Pd black decrease to 10.6 mA mg−1, while the PdCu ANCs shows a comparative decrease of 18.37% to 133.2 mA mg−1, together with a nuance crystal structure (Figure S9a, Supporting Information), elemental composition (Figure S9b, Supporting Information), and morphological structure (Figures S10a,b, Supporting Information) change, which further demonstrates that PdCu ANCs are a stable and highly active FAOR electrocatalyst. Meanwhile, the accelerated durability tests (ADTs) further confirm the remarkable FAOR durability and structural robustness of PdCu ANCs (experimental Section).
After 200 cycles of ADTs, the positive oxidation peak current density and oxidation potential of PdCu ANCs did not change obviously, while the negative sweep peak decreased (Figure 4f), suggesting that the catalyst did not suffer obvious poisoning phenomenon after ADTs test, and maintained stable FAOR activity.

In addition to the excellent FAOR performance, PdCu ANCs also exhibit outstanding performance in ORR under alkaline condition. The ORR catalytic performance of PdCu ANCs, commercial Pd black, and commercial Pt black catalysts were evaluated using a rotating ring-disk electrode (RRDE) at 1600 rpm in 0.1 M KOH solution. As shown in Figure 5a,b, the PdCu ANCs holds a better ORR performance with half-wave potentials ($E_{1/2}$) than that of commercial Pt black ($E_{1/2} = 0.852$ V) and Pd black ($E_{1/2} = 0.827$ V) catalysts. The $E_{1/2}$ values of PdCu ANCs surpass a majority of reported Pd-based catalysts toward ORR in alkaline media (Table S2, Supporting Information), highlighting the brilliant ORR activity of PdCu ANCs. From the Tafel plot (Figure 5c), the ORR electrocatalytic activity of PdCu ANCs catalysts were further revealed. A lower Tafel slope of PdCu ANCs (50.8 mV dec$^{-1}$) is definitely superior to that of commercial Pd black (58.6 mV dec$^{-1}$) and Pt black (66.1 mV dec$^{-1}$) catalysts, suggesting a fast ORR kinetics on PdCu ANCs.[68] To get insight into the ORR pathway of the PdCu ANCs, the RRDE measurement was carried out to track the formation yield of peroxide species (HO$_2$%) and number of electron transfer ($n$) during the ORR process. As verified in Figure 5d,e, the yield of HO$_2$% and number of electron transfer of the PdCu ANCs ($n$: 3.92–3.98, HO$_2$%: <3%) are much better than that of Pd black and comparable to that of Pt black, manifesting the ideal four-electron pathway on the PdCu ANCs.[69] For a more objective evaluation, the hydrodynamic voltammograms were recorded at a scan rate of 5 mV s$^{-1}$ over a range of rotation rates of 100–2500 rpm (Figure S11a, Supporting Information).

---

**Figure 4.** Comparison of the formic acid oxidation reaction (FAOR) performances of PdCu ANCs and Pd black. a) Cyclic voltammetry (CV) Curves of PdCu ANCs and Pd black in 0.5 M H$_2$SO$_4$ solution; b) Mass-normalized FAOR curves in N$_2$-saturated 0.5 M H$_2$SO$_4$ + 0.5 M HCOOH solution; c) Tafel plots derived from Figure S7, Supporting Information; d) Turnover frequencies (TOFs); e) CO-stripping curves; f) CV curves before and after accelerated durability tests (ADTs) tests.
Calculations based on the Koutecky–Levich equation result in a transfer electron number per oxygen molecule of 3.96 on the surface of PdCu ANCs (Figure S11b, Supporting Information), further confirming a complete four-electron pathway. These results reveal that PdCu ANCs are favorable ORR electrocatalysts with superior catalytic activity and stability over commercially available catalysts. The electrocatalytic long-term stability as an important factor for ORR performance was performed by i-t chronoamperometry at 0.8 V (Figure 5f). After running for 44 000 s, the PdCu ANCs exhibit 88.6% retention of the initial current density, while only 85.3% and 81.2% retention can be found on the commercial Pt black and Pd black, respectively. Moreover, the PdCu ANCs show an inconspicuous attenuation with only 3 mV negative shift of half-wave potential after stability test, further verifying the admirable stability of the PdCu ANCs (Figure S12, Supporting Information). The excellent stability of PdCu ANCs is mainly attributed to its stable 3D structure. Furthermore, PdCu ANCs also exhibit a half-wave potential of 0.78 V in 0.5 M H2SO4 solution, which is about 20 mV lower than that of Pd black (Figure S13, Supporting Information), indicating that PdCu ANCs possess a certain potential for application in formic acid fuel cells. To further demonstrate the advantages of 3D structure of PdCu ANCs, PdCu alloy nano-branched clusters (PdCu NBCs) were synthesized as a comparison sample for FAOR and ORR tests (Figure S14, Supporting Information). The electrocatalytic results show that PdCu ANCs exhibit significantly improved electrocatalytic activities than those of PdCu NBCs in FAOR and ORR (Figure S15, S16, Supporting Information). Overall, PdCu ANCs exhibit 3.92-fold mass activity toward FAOR and 27 mV half-wave potential advantage towards ORR, out-performing PdCu NBCs catalyst.

On account of the above electrocatalytic results, the excellent bifunctional catalytic performance of PdCu ANCs towards FAOR and ORR can stem from strong 3D porous networked nanostructure, unique Pd-enriched surface and the alloyed PdCu composition. Specifically, i) Robust 3D porous networked nanostructure can not only effectively expose more active sites and facilitate the
transport of electrons and mass along the continuous nanonetworks, thus promoting the fast kinetics of electrochemical reactions, but also possess strong self-supporting ability to effectively inhibit the aggregation, dissolution and Ostwald ripening during electrocatalysis.\(^{[70,71]}\) ii) Unique Pd-enriched surface could effectively tune the electron structure of Pd and lower its d-band centre, thereby improving the adsorption of the intermediate on Pd surface and promoting the selectivity of the direct path.\(^{[73,74]}\)

3. Conclusion

In conclusion, we have developed an efficient and nontraditional cyanogel-induced approach for the synthesis of PdCu ANCs with Pd-enriched surface and 3D structure. It was illustrated that the synthesis of Cu\(_2\)[Pd(CN)\(_4\)]\(_x\)·aH\(_2\)O cyanogel can be achieved for the first time using K\(_2\)[Pd(CN)\(_4\)] and CuCl\(_2\) as metal salt precursors. Electrochemical experiments results shown the PdCu ANCs exhibits favourable performance with satisfactory ECSA, half-wave potential, mass/specific activity and impressive long-term stability in FAOR and ORR, comparable to or even exceeding commercial Pt black and Pd black catalyst. The enhanced FAOR and ORR activity and their strong stability were ascribed to the synergy of the robust 3D networked structure, unique Pd-enriched surface and electronic effect between Pd and Cu. This simple preparation strategy can be applied to the synthesis of other catalysts induced by cyanogel for the further study and design of efficient bifunction fuel cell catalysts.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

Q.L. and Z.L. contributed equally to this work. This work was financially supported by National Natural Science Foundation of China (21275112) and Postgraduate Research & Practice Innovation Program of Jiangsu Province (KYCX22_1551). The authors are grateful for the supports from National and Local Joint Engineering Research Centre of Biomedical Functional Materials and a project sponsored by the Priority Academic Program Development of Jiangsu Higher Education Institutions.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available on request from the corresponding author. The data are not publicly available due to privacy or ethical restrictions.

Keywords

bifunctional electrocatalyses, cyanogels, formic acid oxidation reactions, oxygen reduction reactions, PdCu alloys

Received: April 29, 2022
Revised: July 4, 2022
Published online: July 19, 2022

[1] H. Zhang, D. Li, Q. Li, K. Guo, C. Yu, J. Lin, C. Tang, Y. Huang, Colloids Surf. A 2022, 646, 128947.
[2] Q. Yang, H. Lin, X. Wang, L. Y. Zhang, M. Jing, W. Yuan, C. M. Li, J. Colloid Interface Sci. 2022, 613, 515.
[3] B. Yang, W. Zhang, S. Hu, C. Liu, X. Wang, Y. Fan, Z. Jiang, J. Yang, W. Chen, J. Colloid Interface Sci. 2021, 600, 503.
[4] X. Wang, Y. Zhu, H. Li, J.-M. Lee, Y. Tang, G. Fu, Small Methods 2022, https://doi.org/10.1002/smtd.202200413.
[5] X. Jiang, Y. Xiong, Y. Wang, J. Wang, N. Li, J. Zhou, G. Fu, D. Sun, Y. Tang, J. Mater. Chem. A 2019, 7, 5248.
[6] F. Kong, W. Shi, Y. Song, L. Ren, X. Sun, J. Wang, Adv. Energy Sustainability Res. 2021, 2, 2100025.
[7] T. Wang, Y. Jiang, J. He, F. Li, Y. Ding, P. Chen, Y. Chen, Carbon Energy 2022, 4, 411.
[8] Z. Fang, W. Chen, Nanoscale Adv. 2021, 3, 94.
[9] H. Xu, H. Shang, C. Wang, Y. Du, Small 2021, 17, 2005092.
[10] Z. Li, H. Li, M. Li, J. Hu, Y. Liu, D. Sun, G. Fu, Y. Tang, Energy Storage Mater. 2021, 42, 118.
[11] Y. Liu, C. Wang, W. Wang, R. Guo, W. Bi, Y. Guo, M. Jin, Nanoscale 2019, 11, 14828.
[12] N. Ye, Y. Bai, Z. Jiang, T. Fang, Electrochimica Acta 2021, 383, 133635.
[13] S. Yang, X. Yang, X. Tong, N. Yang, Adv. Energy Sustainability Res. 2021, 2, 2100058.
[14] M. Zhang, J. Zhu, R. Wan, B. Liu, D. Zhang, C. Zhang, J. Wang, J. Niu, Chem. Mater. 2022, 34, 959.
[15] S. Yang, J. Yang, Y. Chung, Y. Kwon, Int. J. Hydrogen Energy 2017, 42, 17211.
[16] Z. Wu, D. Caracciolo, Y. Maswadeh, J. Wen, Z. Kong, S. Shan, J. Vargas, S. Yan, E. Hopkins, K. Park, A. Sharma, Y. Ren, V. Petkov, L. Wang, C. J. Zhong, Nat. Commun. 2021, 12, 859.
[17] M. Pang, M. Yang, J. Yan, B. Zhang, L. Zang, A. Fu, P. Guo, Langmuir 2022, 38, 4287.
[18] M. Flores Espinosa, T. Cheng, M. Xu, L. Abatemarco, C. Choi, X. Pan, W. Goddard, Z. Zhao, Y. Huang, ACS Energy Lett. 2020, 5, 3672.
[19] Z. Li, M. Li, X. Wang, G. Fu, Y. Tang, Nanoscale Adv. 2021, 3, 1813.
[20] M. Gholesnejad, F. Khosravi, M. Afzali, J. M. Sansano, C. Nájera, Catal. Sci. Technol. 2021, 11, 2652.
[21] W. Tang, L. Zhang, G. Henkelman, J. Phys. Chem. Lett. 2011, 2, 1328.
[22] T. Zeng, X. Meng, H. Huang, L. Zheng, H. Chen, Y. Zhang, W. Yuan, L. Y. Zhang, Small 2018, 18, 2107623.
[23] M. Li, F. Tian, T. Lin, L. Tao, X. Guo, Y. Chao, Z. Guo, Q. Zhang, L. Gu, W. Yang, Y. Yu, S. Guo, Small Methods 2021, 5, 2100154.
[24] D. Zhang, J. Cao, X. Zhang, Z. Zeng, N. Insin, J. Qin, Y. Huang, Adv. Energy Sustainability Res. 2022, 3, 2100183.
[25] P. Rao, J. Luo, J. Li, W. Huang, W. Sun, Q. Chen, C. Jia, Z. Liu, P. Deng, Y. Shen, X. Tian, Carbon Energy 2022, https://doi.org/10.1002/cey2.192.
[26] X. Li, Y. Liu, J.-J. Zhang, B. Yan, C. Jin, J. Dou, M. Li, X. Feng, G. Liu, Chem. Mater. 2022, 34, 1385.
[27] C. Wang, Z. Zhang, G. Yang, Q. Chen, Y. Yin, M. Jin, Nano Lett. 2016, 16, 5669.
[28] Z. Wang, Z. Dai, S. Wang, H. Zhang, W. Tian, Y. Xu, X. Li, L. Wang, H. Wang, Chem. Eng. J. 2021, 416, 134476.
[29] Y. Wang, H. Lv, L. Sun, X. Guo, D. Xu, B. Liu, ACS Appl. Mater. Interfaces 2021, 13, 17959.
[30] C. Wang, X. Li, L. Jin, P. H. Lu, C. Dejoie, W. Zhu, Z. Wang, W. Bi, R. E. Dunin-Borkowski, K. Chen, M. Jin, Nano Lett. 2019, 19, 6363.
[31] F. Zhao, L. Zheng, Q. Yuan, X. Yang, Q. Zhang, H. Xu, Y. Guo, S. Yang, Z. Zhou, L. Gu, X. Wang, Adv. Mater. 2021, 33, 2103383.
[32] F. Gao, Y. Zhang, B. Zou, F. Jiang, Z. Li, Y. Du, J. Colloid Interface Sci. 2022, 610, 271.
[33] Z. Yu, S. Xu, Y. Feng, C. Yang, Q. Yao, Q. Shao, Y. F. Li, X. Huang, Nano Lett. 2021, 21, 3805.
[34] F. Wang, S. Wang, D. Wu, H. Huang, W. Yuan, L. Y. Zhang, Appl. Surf. Sci. 2021, 537, 147860.
[35] K. Zhang, C. Wang, H. You, B. Zou, S. Guo, S. Li, Y. Du, Chem. Eng. J. 2022, 438, 135666.
[36] L. Zhang, F. Wang, S. Wang, H. Huang, X. Meng, Y. Ouyang, W. Yuan, C. Guo, C. M. Li, Adv. Funct. Mater. 2020, 30, 2003933.
[37] C. Lian, Y. Cheng, L. Chen, X. Han, X. Lei, Y. Liu, Y. Wang, ChemComm 2018, 54, 7058.
[38] X. Li, H. You, C. Wang, D. Liu, R. Yu, S. Guo, Y. Wang, Y. Du, J. Colloid Interface Sci. 2021, 591, 203.
[39] H. M. An, Z. L. Zhao, L. Y. Zhang, Y. Chen, Y. Y. Chang, C. M. Li, ACS Appl. Mater. Interfaces 2018, 10, 41293.
[40] H. Yang, Y. Wu, Z. Zhuang, Y. Li, C. Chen, Chinese J. Chem. 2021, 40, 515.
[41] F. Gao, Y. Zhang, F. Ren, Y. Shiraiishi, Y. Du, Adv. Mater. 2020, 30, 2000253.
[42] H. Zhang, H. Xu, L. Jin, C. Chen, C. Wang, T. Song, Y. Du, J. Colloid Interface Sci. 2019, 556, 360.
[43] H. Xu, B. Yan, K. Zhang, J. Wang, S. Li, C. Wang, Y. Shiraiishi, Y. Du, P. Yang, J. Colloid Interface Sci. 2017, 505, 1.
[44] P. Yu, H. Xu, L. Jin, C. Chen, H. Shang, Q. Liu, Y. Du, J. Colloid Interface Sci. 2019, 555, 195.
[45] J. Wang, Z. Liu, X. Yang, P. Cheng, C. Yan, Nanomaterials 2021, 11, 3382.
[46] Z. Liu, G. Fu, J. Li, Z. Liu, L. Xu, D. Sun, Y. Tang, Nano Res. 2018, 11, 4686.
[47] H. Liu, X. Liu, Y. Li, Y. Jia, Y. Tang, Y. Chen, Nano Res. 2016, 9, 3494.
[48] X. Liu, Y. Zhang, M. Gong, Y. Tang, T. Lu, Y. Chen, J. M. Lee, J. Mater. Chem. A 2014, 2, 13840.
[49] H. Liu, J. Li, L. Wang, Y. Tang, B. Y. Xia, Y. Chen, Nano Res. 2017, 10, 3324.
[50] Z. Liu, X. Yang, L. Cui, Z. Shi, B. Lu, X. Guo, J. Zhang, L. Xu, Y. Tang, Y. Xiang, Part. Part. Syst. Char. 2018, 35, 1700366.
[51] Z. Liu, G. T. Fu, L. Zhang, X. Y. Yang, Z. Q. Liu, D. M. Sun, L. Xu, Y. W. Tang, Sci. Rep. 2016, 6, 32402.
[52] E. Ruiz, S. Alvarez, R. Hoffmann, J. Bernstein, J. Am. Chem. Soc. 1994, 116, 8207.
[53] S. Kaye, J. Long, J. Am. Chem. Soc. 2005, 127, 6506.
[54] K. W. Chapman, P. J. Chupas, C. J. Kepert, J. Am. Chem. Soc. 2006, 128, 7009.
[55] Z. Liu, X. Yang, B. Lu, Z. Shi, D. Sun, L. Xu, Y. Tang, S. Sun, Appl. Catal. B 2019, 243, 86.
[56] K. Ashley, S. Pons, Chem. Rev. 1988, 88, 673.
[57] W. Zhang, X. Zhu, X. Chen, Y. Zhou, Y. Tang, L. Ding, P. Wu, Nanoscale 2016, 8, 9828.
[58] Y. Chen, Y. Yang, G. Fu, L. Xu, D. Sun, J.-M. Lee, Y. Tang, J. Mater. Chem. A 2018, 6, 10632.
[59] Z. Li, Y. Chen, G. Fu, Y. Chen, D. Sun, J. M. Lee, Y. Tang, Nanoscale 2019, 11, 2974.
[60] Y. Li, C. Zhang, C. Du, Z. Zhuang, F. Zheng, P. Li, Z. Zhang, W. Chen, Sci. China Chem. 2019, 62, 378.
[61] H. Yu, Z. Wang, D. Yang, X. Qian, Y. Xu, X. Li, H. Wang, L. Wang, J. Mater. Chem. A 2019, 7, 12526.
[62] A. C. Thompson, X-Ray Data Booklet, Lawrence Berkeley National Laboratory, University of Columbia, Berkeley, USA 2009.
[63] R. G. Mariano, K. Mckelvey, H. S. White, M. W. Kanan, Science 2017, 358, 1187.
[64] Y. Xiong, W. Ye, W. Chen, Y. Wu, Q. Xu, Y. Yan, H. Zhang, J. Wu, D. Yang, RSC Adv. 2017, 7, 5800.
[65] X. Li, X. Wang, M. Liu, H. Liu, Q. Chen, Y. Yin, M. Jin, Nano Res. 2017, 11, 780.
[66] C. Rettenmaier, R. M. Aran-Ais, J. Timoshenko, R. Rizo, H. S. Jeon, S. Kuhl, S. W. Chee, A. Bergmann, B. Roldan Cuenya, ACS Catal. 2020, 10, 14540.
[67] X. Qiu, H. Zhang, P. Wu, F. Zhang, S. Wei, D. Sun, L. Xu, Y. Tang, Adv. Funct. Mater. 2017, 27, 1603852.
[68] F. Zheng, C. Zhang, X. Gao, C. Du, Z. Zhuang, W. Chen, Electrochimica Acta 2019, 306, 627.
[69] F. Zheng, Y. Fan, W. Chen, ACS Appl. Interfaces 2021, 13, 38170.
[70] L. Zhang, D. Lu, Y. Chen, Y. Tang, T. Lu, J. Mater. Chem. A 2014, 2, 1252.
[71] C. Ge, R. Wu, Y. Chong, G. Fang, X. Jiang, Y. Pan, C. Chen, J.-J. Yin, Adv. Funct. Mater. 2018, 28, 1801484.
[72] D. He, D. He, J. Wang, Y. Lin, P. Yin, X. Hong, Y. Wu, Y. Li, J. Am. Chem. Soc. 2016, 138, 1494.
[73] Z. Teng, M. Li, Z. Li, Z. Liu, G. Fu, Y. Tang, Mater. Today Energy 2021, 19, 00596.
[74] X. Wang, Y. Tang, J.-M. Lee, G. Fu, Chem Catal. 2022, 2, 967.