Integrating Carbon Dots with Porous Hydrogels to Produce Full Carbon Electrodes for Electric Double-Layer Capacitors

Ji-Shi Wei,[†] Tian-Bing Song,[†] Peng Zhang, Ze-Yang Zhu, Xiang-Yang Dong, Xiao-Qing Niu, and Huan-Ming Xiong*



ABSTRACT: As a class of electrode materials for electric double-layer capacitors (EDLCs), carbon dots (CDs) are able to enlarge specific surface areas, fabricate hierarchical pores, and graft pseudocapacitive groups, leading to additional capacities and superior energy densities. In this work, the commercial polyacrylamide gel (PAMG) is used as a good host for CDs, which has continuously interconnected pores, a cross-linked network, and good swelling capacity so as to form continuous conductive carbon skeleton. After a one-step calcination–activation treatment, CDs are fused onto the final carbon architecture to form a series of porous carbon materials with specific functional groups. Different kinds of CDs, including the oxygen-doped, the nitrogen-doped, and the oxygen, nitrogen co-doped ones, are employed to prepare such carbon materials and tested, respectively. All of these materials have high specific surface areas, well-balanced pore size distributions, high conductivity, abundant superficial functional groups, and good wettability. When they are assembled as electrodes in EDLC, they exhibit remarkable performances, such as specific capacitance of 401-483 F g⁻¹, rate stability over 75% (1–30 A g⁻¹), energy density of 17–23 Wh kg⁻¹, and cycling life of nearly 100%. These results prove that our method, calcination–activation on the CDs–porous (hydro)gel composites, is a universal route of preparing good carbon electrode materials for electrochemical energy storage.

KEYWORDS: carbon dots, porous (hydro)gel, host-guest structure, carbon electrode material, electric double-layer capacitors

1. INTRODUCTION

Porous carbon materials, as the conventional electrodes for electric double-layer capacitors (EDLCs), have obtained wide recognition because of their great advantages in large surface areas, hierarchical porous structures, and abundant functional groups.¹ In general, the above factors are key points to the electrochemical performances of electrodes, but they should be optimized to reach the desired performance results.² But, in most cases, carbon materials are not well designed or not easily adjusted, because their contents are often limited by uncertain compositions of precursors such as biomass,³ and their porous structures are usually limited by traditional processes such as hard/soft templated methods.⁴ As a result, the final carbon products cannot always meet the prospective requirements. However, this situation has changed when carbon dots (CDs) are employed as EDLC electrode materials.⁵

As a new class of zero-dimensional carbon nanomaterials, CDs always possess at least one dimension less than 10 nm and fluorescence as their instinct properties, which include graphene quantum dots (GQDs), carbon nanodots (CNDs), and polymer dots (PDs). Nowadays, CDs have become a focus in electrochemical research.⁶ CDs are much different from the other carbon nanomaterials such as graphene and carbon nanotubes, because they have unique structures of graphitic

cores, amorphous shells, and various organic groups, and special merits including adjustable surface states, good dispersion in solvents, and low cost for production.⁷ Recently, CDs-based composites performed well in both Zn–air batteries,⁸ alkaline aqueous batteries,⁹ and lithium/sodium ion batteries.¹⁰ Related investigations disclosed that CDs are able to provide excellent interfaces between electrolytes and electrodes, facilitating electrons/ions transference, and improving surface reactions.¹¹ All of these achievements indicate a promising future of CDs in this field, and their applications in electrochemical energy storage devices are worthy of wide exploration.

Specifically, CDs have incomparable advantages and great potential in EDLC. First, CDs have wide precursor sources and facile synthetic routes, which ensure CDs a kind of cheap and reliable material.¹² Second, the surface states of CDs are

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controllable, especially bottom-up methods via specific molecules or oligomers.^{6,13} Such routes can produce abundant surface defects, electron-rich regions and specific surface compositions to CDs, so as to break the limitation of a typical ions adsorption/desorption process and lead to higher energy densities for practical circumstances.¹³ According to our previous research, all requirements of carbon-based electrodes such as abundant functional groups, good surface wettability, and tunable porous structures can be met by CDs simultaneously.⁶ Furthermore, the well-designed CDs through specific precursors and preparation routes could provide associated functions, which can effectively rebuild the electrode materials in different sides, such as surface morphology or surface electron distribution.^{7,14} Nevertheless, only employing CDs could not produce ideal electrode materials because such nanoparticles are apt to lose their surface activities after aggregation or calcination.⁷ Therefore, it is very important to find a suitable framework material as CDs carriers. This framework should be some kind of porous carbon with high graphitization degree and tight adhesion to CDs. In addition, the composition and structure of CDs can be adjusted for practical requirements, and these CDs should maintain their properties after integration with the framework materials.

In the present research, we find the commercial polyacrylamide gel (PAMG) is a good host for CDs. It has continuously interconnected pores, a cross-linked network, and good swelling capacity, which can form a continuous conductive carbon skeleton with large surface area and a hierarchically porous structure after calcination. When a PAMG is put into the aqueous solution of CDs, CDs will be adsorbed completely and dispersed homogeneously in the PAMG. After a one-step calcination-activation, CDs are fused onto the final carbon architecture to form a new type of carbon materials, which have high specific surface areas (SSAs), wellbalanced pore size distributions, high conductivity, abundant superficial functional groups, and good wettability. We believe this strategy is a universal route for preparing high-performance carbon electrodes. Because CDs have abundant functional groups on surfaces, they are apt to combine with (hydro)gel through the reswelling process. The host gels and the guest CDs are miscible and compatible; they will fuse together during calcination to form the desired porous carbon structures. To study the relationship between their composition and their electrochemical properties, CDs are synthesized with oxygen dopant, nitrogen dopant, and both of them in advance, respectively. When the final products are assembled as electrodes in EDLC, they exhibit remarkable performances, including specific capacitance, rate ability, energy density (symmetric devices), cycling life, and all other aspects. The above results demonstrate CDs could be fully utilized via the combination of CDs and (hydro)gel, which makes it possible to control the nano-/microstructures and the final capacitive performance of carbon electrodes. Accordingly, related materials and methods will offer a new strategy, namely, the combination of designed CDs and (hydro)gels for the precursors of carbon-based EDLC electrodes.

2. EXPERIMENTAL SECTION

2.1. Preparation of Different CDs. *O-Doped CDs (OCDs).* A 0.1 g amount of citric acid (AR), 300 μ L of ethylenediamine (AR), and 500 μ L of deionized water were mixed and added into the Teflonlined stainless-steel autoclave. Such autoclave was put into an oven and maintained at 160 °C for 4 h. After the reaction, 5 mL of deionized water was added into the reactants to form a clear brown solution. The solid CDs powder was obtained by adding ethanol into the solution and collecting the precipitate via centrifugation. The precipitate was washed by ethanol for several times and further dried in a vacuum oven at 40 °C for 24 h. The final product was a dark brown powder (with yield of 70–75%).

N-Doped CDs (NCDs). A concentrated PEI solution (containing 0.5 g of PEI) was diluted in 20 mL of water and then 0.5 mL of hydroquinone solution (1 mg mL^{-1}) was added. After stirring at room temperature for 1 day, the color of the mixed solution changed from colorless to pale yellow. Then the solution was transferred into a Teflon-lined stainless-steel autoclave with a volume of 100 mL. The sealed autoclave was put into an oven and maintained at 160 °C for 5 h. After the hydrothermal reaction, the as-prepared solution was purified via dialysis membrane (Spectrum; MW cutoff, 12000). Then, the CDs solution was freeze-dried for further experiments.

O,N Co-doped CDs (ONCDs). A 3.25 g amount of CA and a concentrated PEI solution (containing 0.5 g of PEI) were dissolved in 5 mL of deionized water and then transferred into a Teflon-lined stainless-steel autoclave. The sealed autoclave was put into an oven and maintained at 160 °C for 5 h. After hydrothermal reactions, the resulting solution was purified via dialysis membrane (Spectrum; MW cutoff, 3500). The purified CDs solution was also freeze-dried for further experiments.

2.2. Preparation of Hydrogel and CDs/Hydrogel-Based Carbons. A 1.2 g amount of acrylamide was dissolved in 10 mL of water; then 6 mg of N,N'-methylenebis(acrylamide) and 20 μ L of N,N,N,N-tetramethylethylenediamine were added in the solution. After 7 mg of APS was added subsequently, such solution turned into hydrogel within 10 min. The hydrogel was freeze-dried to remove the adsorbed water and then immersed into an aqueous solution containing CDs, NaCl, and ZnCl₂ for swelling. The weights of the CDs powder, hydrogel, NaCl, and ZnCl₂ are the same in such a precursor. Afterward, the mixture was freeze-dried and the impregnated material was calcinated at 300 $\,^{\circ}\mathrm{C}$ in the tube furnace for 1 h with a heating rate of 5 °C min⁻¹. Thereafter, the temperature was raised to 800 °C at a rate of 2 °C min⁻¹ and maintained at 800 °C for 2 h. The whole calcination process was under nitrogen atmosphere with a flow rate of 60 mL min⁻¹. The final products were first washed with HCl aqueous solution $(1 \text{ mol } L^{-1})$ to remove inorganic salts (NaCl and ZnCl₂) and then washed with deionized water repeatedly. At last, related products (porous carbons) were dried in the vacuum oven at 80 $\,^\circ \! C$ for 24 h. These products are named as HPC (hierarchical porous carbon, the CDs-free sample as control), OCD/ HPC (synthesized with O-doped CDs), NCD/HPC (synthesized with N-doped CDs), and ONCD/HPC (synthesized with O,N-codoped CDs).

Characterizations and electrochemical measurements are deposited in the Supporting Information (SI).

3. RESULTS AND DISCUSSION

CDs are synthesized and doped with different elements by changing precursors, which are designated as OCDs, NCDs, and ONCDs according to the doped elements, respectively (Scheme 1). These CDs are dispersed in an aqueous solution of NaCl and ZnCl₂ with appropriate concentrations and then absorbed together by PAMG. The as-prepared hybrid hydrogels present the same colors of fluorescence as the original CDs solutions under both visible light and UV light (Figure 1A,B), indicating that CDs maintain their original features after incorporation with PAMG. The UV-vis absorption curves of different CDs solutions contain two typical absorption bands in the UV region, corresponding to the electron transitions from the π (or n) orbitals to the π^* orbitals.¹⁵ The photoluminescence (PL) spectra of all CDs samples exhibit a broad peak under different excitation light in Figure S1 (SI). The above optical properties confirm that the as-prepared CDs are similar to those typical CDs in our

Scheme 1. HPC Materials Prepared with Commercial PAMG and Different CDs



previous works.¹⁶ Since CDs are miscible with PAMG, they can be dispersed homogeneously in the hybrid gels. It should be mentioned that both NaCl and ZnCl₂ are important for preparing the final hierarchical porous carbon materials. During the subsequent calcination, NaCl forms nanocrystals to support the main structure, while ZnCl₂ helps generate pores by corroding carbon mildly.¹⁷ In this way, the final HPC materials have large surface areas and stable porous structures. When CDs are incorporated, the obtained OCD/HPC, NCD/ HPC, and ONCD/HPC have similar pore volumes (0.504-0.591 cm³ g⁻¹) and specific surface areas $(1001-1168 \text{ m}^2 \text{ g}^{-1})$ with the CDs-free HPC (Table S1, SI). All samples show similar nitrogen adsorption-desorption isotherms and pore size distribution curves in Figure 2A,B, respectively. It is known that the micropores are beneficial for ions storage, while the mesopores are favorable for ions' accessibility.¹¹ Both the surface area proportions and the pore volume proportions

between mesopores and micropores in different samples are also similar for all HPC materials (Figure 2C,D). And, thus, the influence from carbon skeleton structures can be excluded when comparing HPC properties. Similarly, SEM images also illustrate the sponge-like porous structure for all HPC samples, with cross-linked networks in Figure 3A-D. The intricate morphologies observed via high-resolution transmission electron microscopy (HRTEM) are shown in Figure 3E-H, where CDs can be found on the carbon skeleton with a size distribution of 3-10 nm. For example, the sizes of N-doped CDs on the carbon substrate are about 5-6 nm (Figure 3 G, inset), while the corresponding CDs precursors have average particle sizes of about 10 nm (Figure S2, SI), indicating that PEI derived CDs are actually carbonized polymer dots, which will shrink during calcination.^{13,14} This phenomenon is similar to that of O,N-co-doped CDs. In brief, our calcinationactivation method has combined CDs and carbon skeletons tightly, which produces a new kind of composites with synergistic effects of two precursors. The XRD (X-ray diffraction) patterns of all HPC samples are shown in Figure 4A, which exhibit the typical (002) and (101) peaks as graphitization characteristics.¹⁹ The FTIR (Fourier transform infrared spectroscopy, Figure 4 B) curves of all HPC and CD/ HPC samples show typical bands at 3450, 1695, 1640, and 1170 cm⁻¹ corresponding to the -OH, C=O, C=C, and C-O–C, respectively. $^{20-23}$

To distinguish the intricate differences between these samples in surface compositions, more detailed element compositions are studied by XPS (X-ray photoelectron spectroscopy, Figure 5A-D and Figure S3, SI) measurements. Since both CDs and the carbon framework HPC have carbon and oxygen elements, the comparison between CDs-free HPC and CDs/HPC focus on nitrogen. In general, the N 1s spectra can be deconvoluted into four peaks corresponding to pyridine-type nitrogen (N-6; BE = 398.1 eV), pyrrole-type nitrogen (N-5; BE = 400.1 eV), quaternary-type nitrogen (N-Q; BE = 401.5 eV), and oxidized nitrogen (N-X; BE = 403) eV), respectively.²⁴ It is clear that all samples exhibit similar C and O bands, while the N compositions in NCD/HPC and ONCD/HPC are significantly larger than the other samples (Table S2, SI). It is well-known that the heteroelements such as nitrogen and phosphorus are apt to be lost when the carbon material precursors are calcined at high temperatures. For example, the CDs-free HPC only has a nitrogen content of 0.99 wt %, though it is derived from polyacrylamide whose



Figure 1. (A) Digital photographs of PAMG (1) and CDs/PAMG mixtures (2–4, OCDs/PAMG, NCDs/PAMG and ONCDs/PAMG, respectively) under sunlight. (B) Same samples under UV light.

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Figure 2. (A) Nitrogen adsorption-desorption isotherms and (B) pore size distributions calculated by the DFT method. (C, D) Proportions of meso-/micropores between different samples.



Figure 3. FESEM images of (A) HPC, (B) OCD/HPC, (C) NCD/HPC, and (D) ONCD/HPC. FETEM images of (E) HPC, (F) OCD/HPC, (G) NCD/HPC (insert: size distribution of carbon dots), and (H) ONCD/HPC.



Figure 4. (A) FTIR spectra and (B) XRD patterns of different samples.

nitrogen content is about 34 wt %. In addition, these CDs themselves have nitrogen contents of 3.36, 9.52, and 7.13 wt % (Table 1) before calcination, respectively. However, when CDs

are incorporated, the obtained CDs/HPC after calcination have nitrogen contents of 1.87, 5.12, and 3.91 wt %, respectively (Table S2). From the results of Table S2, CDs



Figure 5. XPS spectra of N element in (A) HPC, (B) OCD/HPC, (C) NCD/HPC, and (D) ONCD/HPC. (E) Schematic comparison between the modified (below) and the unmodified (up) surfaces.

could supply functional groups, which can increase the content of heteroelements effectively. This means the nitrogen contents are much more stable in CDs than those in many other nitrogen-containing precursors. More importantly, this result proves that our strategy is able to produce carbon materials with not only a high degree of graphitization but also a high degree of heteroelements doping, both of which are desired by EDLC devices. This control experiment well-proves that CDs are effective and stable carriers for both functional groups and heteroelements when the carbon materials should be treated at high temperature (Figure 5E). In this way, hybrid carbon materials with both high graphitization degree and rich surface groups are prepared successfully. As an obvious effect of rich surface groups, the wetting property of HPC is significantly enhanced by incorporation with CDs. The water contact angle on HPC surfaces is decreased from 17.1° to 9° after loading CDs. On the basis of all results in Figure S4, nitrogen functional groups introduced by CDs are able to increase the wetting property, which accelerates the ions diffusion from the electrolyte toward the electrode surface, reduces the contact resistance between the electrode and the electrolyte, and improves EDLC performances at high current densities.¹

Cyclic voltammetry (CV) measurements are carried out at different sweep rates to examine the capacitive reactions of each sample (Figure 6A and Figure S5, using saturated Hg/ Hg_2SO_4 electrode as the reference electrode). The shapes of the CV curves in the H_2SO_4 solution are almost square, meaning that such ideal capacitive behaviors are based on electrostatic attractions.²⁵ As a character of the faradaic pseudocapacitance, a pair of symmetrical, wide peaks can be observed in each curve of CDs/HPC samples,²⁶ which refer to the reactions between hydrated protons and surface groups. Hence, all CDs/HPC samples are able to combine plenty of protons for external capacitance through their numerous surface groups brought by CDs. Galvanostatic chargedischarge (GCD) experiments are also employed to investigate the specific capacitance performances of these samples more accurately. As shown in Figure 6B, GCD curves exhibit symmetric triangular shapes without any obvious Ohmic drops between -0.6 and +0.4 V versus the saturated Hg/Hg₂SO₄ electrode. Compared with CDs-free HPC, specific capacitances of CDs/HPC samples exhibit significant enhancement of 33.8-60.4% (Figure 6C). Particularly, the optimal capacitance of ONCD/HPC even reaches 483 F g⁻¹ at 1 A g⁻¹ (Table S3). The rate performances of all samples are investigated at different current densities from 1 to 30 A g^{-1} (Figure 6D). Retention rates of all samples are over 75%, and the optimal ONCD/HPC has a retention rate up to 80%. These samples exhibit slow variation of specific capacitances, indicating their excellent retention stabilities. More importantly, all samples show exceptional cycling stability after 10000 cycles at different current densities (Figure S6).

Electrochemical impedance spectroscopy (EIS) is utilized to study the capacitive characteristics of our samples in another way (Figure 7A,B and Table S4, SI). The steep linear Nyquist curve in the low-frequency region indicates a nearly ideal capacitive performance, while the semicircle in the highfrequency region represents the conductivity of the active materials and the electrolyte.²⁷ CDs/HPC samples have lower interface resistances than CDs-free HPC, in accord with the results of contact angle tests. That is to say introduction of CDs into HPC is also favorable for the electrolyte penetration, which not only enhances the surface wettability by electrolytes but also improves the conductivity of the electrode materials. Evolution of $C'(\omega)$ and $C''(\omega)$ is based on formulas S2–S4 (see Electrochemical Measurements, SI).²⁸ It is known that the operating frequency (f_0 , frequency at which capacitance is 50% of the maximum) and the characteristic relaxation time constant (τ_0) are the significant quantitative indicators for the reversible charging/discharging rates of the electrodes.²⁹ The optimal sample ONCD/HPC has an operating frequency of 0.32 Hz, higher than those of NCD/HPC (0.14 Hz), OCD/ HPC (0.38 Hz), and especially HPC (0.09 Hz). Correspondingly, their characteristic relaxation times are 3.2, 7.3, 2.6, and 11.5 s, respectively (Table S4, SI), confirming that CDs have

Table 1. Surface Atomic Percentage of Nitrogen and Oxygen Derived from XPS Results (Carbon Dots, CDs)

	species concn (wt %)			N 1s (wt %) ^a			O 1s (wt %) ^a		
sample	C 1s	N 1s	O 1s	N-6	N-5	N-Q	С-ОН	С-О-С	СООН
OCDs	75.03	3.36	21.61	0.86	0.85	1.65	4.51	8.59	8.51
NCDs	89.28	9.52	1.20	2.12	2.23	5.10	0.63	0.57	
ONCDs	72.56	7.13	20.32	1.20	1.23	4.73	4.89	7.38	8.05

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^{*a*}N–X and C=O not determined.

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Figure 6. Electrochemical performances of different materials in 1 mol L^{-1} H₂SO₄ aqueous solution (measured by the three-electrode system, using the saturated Hg/Hg₂SO₄ as reference electrode). (A) CV curves at a scan rate of 10 mV s⁻¹. (B) GCD curves at a current density of 1 A g⁻¹. (C) Specific capacitances at a current density of 1 A g⁻¹. (D) Rate performances.



Figure 7. EIS results of different materials. (A) Nyquist impedance plot. (B) normalized imaginary part of capacitances versus the frequency.

played an important role in enhancing the electric field response abilities of electrodes.

EDLCs are assembled to evaluate the as-prepared porous carbon materials for practical applications by simultaneously using them as both the positive electrode and the negative electrode. In a neutral aqueous solution containing 2 mol L⁻¹ Na_2SO_4 , CV curves (Figure 8A) and GCD curves (Figure 8B) of such a symmetric device are recorded at various scan rates and current densities in the potential range of 0-1.5 V. No signals can be observed as oxygen or hydrogen evolution peaks in the CV curves which only exhibit typical capacitor behaviors.³⁰ Besides, highly symmetrical charge-discharge curves imply a good Coulombic efficiency. Owing to the effective integration between CDs and carbon frameworks, the active sites keep intact during cycling tests and the retention rates of all samples are nearly 100% at different current densities (Figure 8C). In addition, power density and energy density are two key parameters to evaluate the performances of EDLC. According to formulas S6 and S7 (SI), these symmetric EDLCs deliver energy densities of 17-23 Wh kg⁻¹, which are comparable to lead acid batteries. Even at a high power density over 11000 W kg⁻¹, such EDLCs still can deliver energy densities of 6.9-13.5 Wh kg⁻¹ (Figure 8D). This result is superior over the reported performances of many other

hydrogels- or CDs-based materials, such as graphene hydrogel-like carbon (17.9 Wh kg⁻¹),³¹ peanut-shell-like porous carbon aerogels (21.53 Wh kg⁻¹),³² and carbon quantum dots/ activated carbon (13.47 Wh kg⁻¹),³³ etc.^{34–38} (Table S5, SI).

4. CONCLUSIONS

We invent a facile and efficient strategy to fabricate highperformance carbon electrodes for EDLCs. Through a onestep calcination-activation, CDs fuse with PAMG effectively to form various doped porous carbons. Detailed measurements show that such carbon materials possess cross-linked graphitized skeletons and activated functional groups from CDs. Those typical requirements for EDLC electrode such as high specific surface area, well-balanced pore size distribution, high conductivity, abundant superficial functional groups, and good wettability are realized perfectly in one material. Particularly, such carbon materials have remarkable specific capacitances over 400 F g^{-1} at 1 A g^{-1} , and the optimal ONCD/HPC capacitance even reaches 483 F g^{-1} . In addition, the superior rate and cycling stability highlight their comprehensive advantages. After being assembled in a practical EDLCs, they exhibit both high energy density $(23.0 \text{ Wh kg}^{-1})$ and high power density (11300 W kg^{-1}), meaning that such EDLCs has combined both merits of batteries and super-

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Figure 8. Electrochemical performances of the symmetric EDLC using aqueous solutions as electrolyte. (A) CV curves at scan rates of 10 mV s⁻¹. (B) GCD curves at current densities of 1 A g⁻¹. (C) Cycle stabilities of different samples at various current densities. (D) Ragone plots of different samples.

capacitors. Our present work confirms that CDs and porous carbon skeletons can produce a new kind of composite materials with excellent performances as EDLCs electrodes, and this strategy will offer a facile way to predesign and adjust both the surface composition and structure of the final carbon electrode materials.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsaem.0c00990.

Materials and methods; PL emission spectra, UV-vis absorption spectra, and HRTEM images; porosity properties; surface atomic percentage (XPS measurements); XPS survey spectra and high-resolution XPS; contact angle measurement images; CV and GCD curves; cycling stabilities; specific capacitance and equivalent circuit parameters; comprehensive comparison with literature devices (PDF)

AUTHOR INFORMATION

Corresponding Author

Huan-Ming Xiong – Department of Chemistry and Shanghai Key Laboratory of Molecular Catalysis and innovative Materials, Fudan University, Shanghai 200438, People's Republic of China; ⊙ orcid.org/0000-0002-3118-942X; Email: hmxiong@fudan.edu.cn

Authors

- Ji-Shi Wei Department of Chemistry and Shanghai Key Laboratory of Molecular Catalysis and innovative Materials, Fudan University, Shanghai 200438, People's Republic of China
- **Tian-Bing Song** Department of Chemistry and Shanghai Key Laboratory of Molecular Catalysis and innovative Materials, Fudan University, Shanghai 200438, People's Republic of China

- **Peng Zhang** Department of Chemistry and Shanghai Key Laboratory of Molecular Catalysis and innovative Materials, Fudan University, Shanghai 200438, People's Republic of China
- **Ze-Yang Zhu** Department of Chemistry and Shanghai Key Laboratory of Molecular Catalysis and innovative Materials, Fudan University, Shanghai 200438, People's Republic of China
- Xiang-Yang Dong Department of Chemistry and Shanghai Key Laboratory of Molecular Catalysis and innovative Materials, Fudan University, Shanghai 200438, People's Republic of China
- Xiao-Qing Niu Department of Chemistry and Shanghai Key Laboratory of Molecular Catalysis and innovative Materials, Fudan University, Shanghai 200438, People's Republic of China

Complete contact information is available at: https://pubs.acs.org/10.1021/acsaem.0c00990

Author Contributions

[†]J.-S.W. and T.-B.S. contributed equally to this work.

Notes

The authors declare no competing financial interest.

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