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Journal of Materials Chemistry A

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ARTICLE

Received 00th January 20xx, Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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The development of high performance non-precious catalysts is still of significance for the promising wide application of proton-exchange membrane fuel cells. In this work, a facile ionothermal polymerization approach was developed to synthesize high active covalent triazine frameworks (CTFs) derived Fe-N_x-C catalysts for mediating the cathodic reaction of fuel cells. The impacts of heating temperature, dosage of $ZnCl_2$, and dinitrile aromatic monomers on oxygen reduction reaction (ORR) activity of Fe-N_x-C catalysts were systematically discussed. High performance CTFs-derived Fe-N_x-C catalysts were successfully obtained, among which the FB7 exhibits an extraordinary ORR performance in 0.1 M HClO₄ aqueous solution. The linear sweep voltammetry (LSV) results show that there are only 14 mV and 25 mV slightly negative shifts of onset potential (E_{onset}) and half-wave potential ($E_{1/2}$) of FB7 comparing with the commercial Pt/C (20 µg Pt cm⁻²). Besides, FB7 also shows better electrochemical stability and methanol-tolerance than that of Pt/C. This outstanding ORR performance of FB7 is attributed to its excellent percolation properties and high density of active sites.

Introduction

The sluggish oxygen reduction reaction is one of the main determinants limiting the commercialization of PEM fuel cells.^{1, 2} Although Pt-based materials have been proven to be the most effective ORR catalysts, their high cost and resource shortage prohibitively limited their wide applications.^{3, 4} To solve this problem from the root, many efforts have been focused on developing non-precious metal (NPM) catalysts with low cost, high activity and significant durability.⁵ Transition metal-nitrogen-carbon (M-N_x-C) materials are regarded as one of the most promising candidates. For M-N_x-C catalysts, high ORR performance was not hard to access under alkaline condition, which displayed higher ORR activity and better durability than that of Pt-based catalysts.⁶⁻⁸ Whereas, the ORR performance of M-N_x-C catalysts still requires more enhancement under PEM fuel cells working condition.⁹

Efficient M-N_x-C catalysts were often obtained by hightemperature pyrolysis of transition metal salt, carbon and nitrogen source. The selection of precursors and pyrolytic procedures determines the types and density of active sites in M-N_x-C catalysts,¹⁰ while the nanostructure of M-N_x-C catalysts determines the accessibility of active sites in the ORR. To ultimately enhance the ORR activity of M-N_x-C catalysts, the specific surface area and

the mesoporosity of M-N_x-C catalysts should be as high as possible to keep each active site accessible and provide facile channels for mass transportation.¹¹⁻¹³ Thus, the regulation of nanostructure of M-N_x-C catalysts becomes a necessary step for the design and synthesis of high performance NPCs. To better tune nanostructure of M-N_x-C catalysts, template methods have been employed widely and successfully to prepare M-N_x-C ORR catalysts with outstanding performance in acidic media. For example, Klaus et al. used Silica colloid as a template and prepared mesoporous Co-Nx-C catalyst which exhibited only 58 mV half-wave potential deviation from Pt/C (20 µg Pt cm⁻²) in acidic media.¹⁴ Feng *et al.* synthesized an efficient Fe-N_x-C catalyst with hollow carbon nanoshells structure by using CdS@mSiO₂ as template, which exhibited only 30 mv half-wave potential negative than Pt/C (20 µg Pt cm⁻²) in acidic media.¹⁰ Although tremendous progresses have been made, silica template method is not very atomic economic and environment friendly because of the extra preparation steps and the utilization of high hazard hydrofluoric acid or harsh strong alkali condition in removing templates.^{15, 16} In this regard, searching for a more affordable and facile strategies to synthesize high performance M-N_x-C catalysts with suitable nanostructure mentioned above is still highly desirable.

Covalent triazine frameworks contain numerous microporous structure by simply bridging with 1,3,5-triazine units as linkage.¹⁷ Similar to phthalocyanine and porphyrin, the nitrogen atoms of CTFs also sitting at the edge of the microporous structure, are capable of coordinating with transitional metals. Moreover, ionothermal polymerization of aromatic nitriles in molten ZnCl₂ is one of the main methods to prepare CTFs, which also offers a facile way to prepare nitrogen-containing carbonaceous framework with tuneable nanostructure by changing ZnCl₂/monomer ratio and

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Electronic Supplementary Information (ESI) available: Detailed synthesis parameter, additional characterization about XRD patterns, Raman spectrums, FT-IR spectrums, XPS spectrums, nitrogen sorption analysis results and supporting data of electrochemical tests. See DOI: 10.1039/x0xx00000x

DOI: 10.1039/C6TA10190A Journal Name

ARTICLE

heating temperature in ionothermal reaction.^{18, 19} Therefore, the CTFs generate by ionothermal method are innate precursors for preparing M-N_x-C ORR catalysts. Hashimoto *et al.* have successfully obtained ORR Cu-CTFs catalysts simply by mixed Cu salts with CTF and conductive carbon nanoparticles through wet impregnation method.



The introduction of Cu in these Cu-CTFs catalysts was proven to be a key for achieving the high ORR performance under neutral condition. $^{\rm 20}$

In case of Fe-N_x-C catalysts, there is a broad consensus that Fe is indispensable to generate active sites with high ORR activity during high temperature treatment.^{21, 22} Based on our knowledges, there are rare reports on the preparation of Fe-CTF materials by the method of ionothermal polymerizing aromatic nitriles with the controllable nanostructure advantage. Herein, we reported a more facile in-situ metal doping strategy to prepare Fe-CTF composites by ionothermal polymerizing aromatic nitrile monomers in molten $ZnCl_2$ containing FeBr₂ (Scheme 1). This strategy could not only avoid the multi-steps of conventional wet impregnation but also retain the advantage of tuneable nanostructure of product without templates.

Experimental

Synthesis of catalysts:

Aromatic nitrile (200 mg), anhydrous $ZnCl_2$ (1-10 equivalent) and anhydrous FeBr₂ (0-1/3 equivalent) were mixed and transferred into quartz tubes in a glove box. Then tubes were evacuated, sealed and heated at 400, 600 or 700 °C for 20 hours. After cooling to room temperature, the dark mixtures were washed with 1 M HCl solution to remove $ZnCl_2$ and unwanted iron compounds. The acid treated carbon materials were further washed with deionized water and tetrahydrofuran, and then dried in vacuum overnight. Table S1 \uparrow shows the detailed synthesis parameters for each sample prepared in this work.

Characterizations:

Fourier-transform infrared spectroscopy (FT-IR) was performed on a PerkinElmer Spectrometer. 4,4'-dicyanobiphenyl was confirmed by 1H NMR. Transmission electron microscopy (TEM) images were obtained on a FEI Tecnai F20 electron microscope diffractometer with a copper target ($\lambda = 0.154$ nm). Micromeritics ASAP2020 was used to collect low-temperature nitrogen adsorption isotherms. Xray photoelectron spectroscopy (XPS) was recorded on a Thermo Scientific ESCALAB. Elemental analysis (EA) was carried out on a VARIO EL CUBE analyzer. Raman spectra was recorded on Renishaw 2000 (excited at 532 nm). Conductivity of samples were obtained on two-probe technique by using Keithley 4200 source meter.

Electrochemical Measurements:

The electrochemical performances of the catalysts were collected by a CHI Electrochemical Station (Model 760e) under rotating disk electrode (RDE) or rotating ring-disk electrode (RRDE) mode. Oxygen reduction reactions were conducted in a three electrode electrochemical cell. A Ag/AgCl electrode in saturated KCl solution and a Pt wire were used as the reference electrode and the counter electrode, respectively. All potentials in this work were calibrated to the reversible hydrogen electrode (RHE) potentials.

Prior to loading catalysts onto the working electrode, the RDE and RRDE were polished with alumina powder and sonicated in a mixture of ethanol and ultrapure water to realize a mirror finish, and finally dried under purified nitrogen flow. The ink of our prepared catalysts was obtained by sonicating the mixture of 4 mg catalyst, 38 μ L (5 wt%) Nafion in alcohol, 600 μ L ethanol and 385 μ L deionized water for 1 hour. Then, the ink was drop coated onto the working electrode (RDE: 20 μ J; RRDE: 25 μ L) with a loading of 0.4 mg cm⁻² and dried at room temperature in air until a uniform thin film catalyst was obtained. Besides, the commercial 20 wt% Pt/C also was drop coated on to RDE and RRDE at a loading of 20 μ g Pt cm⁻² for comparison.

In case of RDE tests, the electrode rotation speed was set to 900 rpm and all LSV behaviors of samples were recorded in 0.1 M HClO₄ at a scan rate of 10 mV s⁻¹. In order to correct the non-Faraday current generated in the catalyst layer, the LSV curve recorded in N₂-saturated 0.1 M HClO₄ was subtracted from the LSV curve recorded in O₂-saturated 0.1 M HClO₄.

In addition to satisfying the same test conditions as RDE, the ring electrode potential of RRDE was set to 1.2 V. The hydrogen peroxide yield $(H_2O_2\%)$ and the number of electrons transferred (n) in the ORR were calculated by (1) and (2) respectively.

$$H_2 O_2 = \frac{2I_R}{N|I_D| + I_R} \times 100$$
(1)
$$n = 4 - \left(2\frac{H_2 O_2(\%)}{100}\right)$$
(2)

where N = 0.37 represents the collection efficiency, I_D represents the disk current, and I_R represents the ring current.

Results and discussion

The CTFs derived Fe-N_x-C catalysts were all prepared by anhydrous $ZnCl_2$ catalysing polymerization of various dinitrile aromatic compounds at the presence of FeBr₂ for 20 hours. After ionothermal polymerization of aromatic nitriles, the mixture was subsequently leaching with dilute hydrogen chloride aqueous solution to remove $ZnCl_2$ and excess iron products. In order to value how the heating temperature influences the properties of Fe-CTFs, catalysts derived from 1,3-dicyanobenzene were synthesized at different temperatures of 400, 600, and 700 °C and labelled as FB4, FB6, and FB7 accordingly. The properties of these catalysts were

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characterized by XRD and Raman spectrum. Fig. S1a⁺ shows the XRD patterns of FB4, FB6 and FB7. Tow broad peaks at $2\theta = 26.5^{\circ}$ and 43° were assignable to the (002) and (101) diffractions of graphitic carbons. The diffraction of (101) gradually emerges as the heating temperature increases. At the same time, the Raman spectra which used to measure the degree of disorder in graphitic structure reveals



Fig. 1 TEM (a), HRTEM (b), SAED (c), HAADF-STEM (d) and EDS mapping images (e-g) of FB7 $\,$



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Fig 2. (a) Current-voltage characteristic and resistances, (b) nitrogen adsorption/desorption isotherms, inset shows the pore size distribution from the BJH model, (c) full XPS spectrum and (d) RDE results (in O_2 -saturated 0.1 M HClO₄ at 900 rpm, with a scan rate of 10 mV s⁻¹) of FB4, FB6 and FB7.

DOI: 10.1039/C6TA10190A

ARTICLE

(Fig. S1b \dagger) that the ratios of I_D/I_G are 2.39, 2.78 and 3.36 for FB7, FB6 and FB4 respectively. Both XRD and Raman analysis manifest that more graphitic structure can be generated by increasing the heating temperature. Transmission electron microscope (TEM) and selected-area electron diffraction (SAED) patterns of FB7 as show in Fig. 1b and 1c confirm the existence of graphitic structure. Moreover, the EDS mapping images of FB7 confirm that iron can be successfully and homogeneously doped across the whole N-C framework of CTFs (Fig. 1f).

The ORR activity of Fe-N_v-C catalysts was examined by LSV at rotating speeds of 900 rpm in an O₂-saturated 0.1 M HClO₄ (Fig. 2d). It's obvious that FB4 prepared at 400 °C almost didn't show any ORR activity. Tremendous increase of ORR activity was observed for both catalysts FB6 and FB7, when the heating temperature was increased from 400 to 600 or 700 °C. Especially, the FB7 exhibits a half-wave potential of 757 mV vs. RHE which is only 25 mV negative than that of Pt/C ($E_{1/2}$ = 782 mV vs. RHE) and superior to most NPMs reported recently (Table S4 \dagger). The increasing ORR activity of FB7, thus, can be attributed to the increasing electron conductivity²³ and large interfacial surface area at high temperature. The ORR also requires the facile transport of O_2 , H^+ , and electrons to catalyst surface though diffusion and conduction.²⁴ Therefore, the carbon supported catalysts have optimum balance of electron conductivity and percolation properties to exhibit best ORR performance. Indeed, the electron conductivity of FB7 is almost 8 factors and 16 times higher than that of FB4 and FB6 (Fig. 2a). It's worth noting that the ionothermal method created more porosity at higher temperature under our experimental temperature range. The nitrogen sorption analysis results of these three catalysts show in Fig. 2b and Table S2 [†]. The BET surface areas of these three catalysts are 609 (FB4), 1585 (FB6) and 2376 m² g⁻¹ (FB7). Calculated by the Barrett-Joyner-Halenda model (BJH), the average pore diameter of FB4 and FB7 are increasing from 2.6 to 3.3 nm. The most importance is that the volume of FB7 (2.1 cm³ g⁻¹) is seven times higher than that of FB4 (0.3 cm³ g⁻¹). These favourable percolation properties of FB7 can significantly facilitate the mass transport in ORR. In addition, as displayed in Fig. 2c, the decrease content of nitrogen has been observed with the increase of heattreated temperature indicates nitrogen-containing species evolved at higher temperature and may triggered the formation of active sites.

In order to investigate the role of Fe species during the process of CTF polymerization which may connect to the ORR activity, two samples B4 and B7 without the presence of any FeBr₂, were obtained according to synthetic procedure of FB4 and FB7 respectively. Fig. S1c⁺ shows FT-IR spectra of B4 and FB4. Both B4 and FB4 have intense bands at 1518 and 2226 cm⁻¹ assignable to triazine rings and nitrile groups. This demonstrates that current reaction condition is impossible to completely turn nitriles into triazine ring. To further investigate the role of Fe, the N 1s XPS data of B4, FB4, B7, and FB7 were listed in Fig. 3. Both FB4 and B4 exhibit N at 398.78 ev (N5) for triazine rings and at 400.39 ev (N6) for

ARTICLE

nitrile groups (Fig. 3a).²⁵ Surprisingly, the concentration of triazine N5 in FB4 is lower than that of B4 (Fig. 3c), which indicates that the Fe species were not in favour of the CTFs polymerization. Moreover, both the results of EA and N1s XPS shows that the ratio of N/C in FB4 is also lower than that of B4 (Table 1), which reveals that Fe also play the role of denitrification. It



Fig. 3 (a) and (b) XPS N1s deconvolution results of B4/FB4 and B7/FB7. (c) content of different N species in B4, FB4, B7 and FB7. (d) RDE results (in O₂-saturated 0.1 M HClO4 at 900 rpm, with a scan rate of 10 mV s⁻¹) of B7 and FB7.

Samples	XPS atomic ratio(%)		EA mass ratio(%)	
	N/C	$\triangle(N/C)$	N/C	∆(N/C)
В4	14.85	0.98	22.81	1.35
FB4	13.87		21.46	
B7	5.82	0.07	9.17	0.19
FB7	5.75		8.98	

Table 1 N/C XPS atomic ratio and EA mass ratio of B4, FB4, B7 and FB7, Δ N/C points to the N/C atomic or mass ratio difference between B4 and FB4, B7 and FB7.

has been reported that the Fe species are capable of catalysing denitrification reaction at high temperature.²⁶ Increasing heating temperature to 700 °C, the denitrification is even worse (Table 1). In fact, the N/C ratio of FB7 is not half of that of FB4. The N1s XPS of FB7 and B7 were deconvoluted into four types of common nitrogen: pyridinic nitrogen (N1, at 398.2ev), pyrrolic nitrogen (N2, at 399.75ev), graphitic nitrogen (N3, at 401ev), and oxidized nitrogen (N4, at ~402.3ev). According to the convolution results (Fig. 3b and 3c), the FeBr₂ is conductive to the formation of pyridinic nitrogen and the denitrification of graphitic nitrogen at 700 °C, but these changes are not obvious. Pyridinic N and pyrrolic N locate at the edge of graphite are capable of coordinating with Fe ions.²⁷⁻²⁹ Two $2p_{3/2}$ peaks at around 711 ev assignable to the N-coordinated Fe²⁺ and Fe $^{3+}$ species were observed in Fe 2p XPS of FB7 (Fig. S3 \dagger). 30 Therefore, part of pyridinic N and pyrrolic N in FB7 may be concerning the formation Fe-N_x active sites. In fact, abundant experiments and theoretical computation results manifested that



Fe-N_x species have a higher efficient activity toward ORR under acidic conditions.³¹⁻³³ Besides, graphitic N and pyridinic-N can both

contribute to the ORR under acid environment.^{34, 35}. Especially, guo

et al. confirmed that pyridinic-N can create active sites for ORR in

Fig. 4 (a) Nitrogen adsorption/desorption isotherms, (b) pore size distribution from the BJH model, (c) content of different N species, (d) RDE results (in O_2 -saturated 0.1 M HClO₄ at 900 rpm, with a scan rate of 10 mV s⁻¹) and (e) current density at 0.15 V and 0.85 V of FB7. FB7-10, FBP7 and FP7.

M HClO₄ with a 183 mV more positive in the half-wave potential (Fig. 3d and Table S3 [†]). The higher ORR activity of FB7 is undoubtedly contributed by the high active species because of Fe. Two types of iron-containing species may exhibit ORR activity under acid condition. One was reported as inorganic iron species encapsulated in the nitrogen-containing carbon layer (Fe@NxCv), while the other were Fe-N_x species embedded in carbon materials. In case of $Fe@N_xC_v$, the Fe species are most likely to affect the activity of catalysts by modifying the electronic structure of the nitrogen-containing carbonaceous framework but not being directly involved in the process of ORR.^{37, 38} But for Fe-N_x species, the consensus is that Fe ions itself act as active site central and catalyse ORR directly and high efficiently.^{39, 40} To further identify the Fe species in our catalysts, the SCN ions blocking ORR test was performed. As shows in Fig S5 †, a sharply potential shift was observed in the LSV curve of catalyst FB7 under the 5 mM NaSCN acid aqueous solution. This behaviour was similar to that of other reported Fe-Nx-C based catalysts under the same test condition, which strongly indicated that the most of ORR activity in FB7 are contributed by the direct Fe-N_x species active sites.^{9, 41}

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As previous stated, the porosity nanostructure is of significance for the percolation properties of high performance ORR catalysts. In addition to catalysing polymerization of dinitrile aromatic monomers, $ZnCl_2$ also play an important role on creating porosity of CTFs. Markus *et al.* proved that a wider pores size distribution can be realized by increasing the equivalent ratio of $ZnCl_2$ /monomer.⁴²



Fig. 5 (a) Tafel ORR plots, (b) H_2O_2 yield and electron-transfer number of Pt/C, FB7. (c) RDE results of FB7 and Pt/C before and after 10000 potential cycles under 0.1 M HClO₄ (saturated with O₂). (d) methanol-tolerance of Pt/C and FB7 tested by the Current–time (I–T) chronoamperometric response in 0.1 M HClO₄.

further investigate impacts of $ZnCl_2$ on ORR activity of catalysts, FB7-1 and FB7-10 were prepared by similar procedures of FB7 with different equivalent ratio of $ZnCl_2/1,3$ -dicyanobenzene (FB7-1: 1/1; FB7: 5/1; FB7-10: 10/1). The nitrogen sorption analysis shows that both FB7 and FB7-10 utilizing high ratio of $ZnCl_2$ exhibit the feature of type IV isotherm with wider mesoporous size and distribution, whereas the FB7-1 displays type I isotherm and relative narrow pores size and distribution (Fig. 4a and 4b).

The limiting current density of FB7 series catalysts is closely proportional to the utilizing amount of ZnCl₂ (Fig. 4d). It's worth noting that the FB7-1 exhibits higher current density at high potential (850 mV vs. RHE) comparing to that of FB7 and FB7-10 (Fig. 4e), whereas it displays lowest current density at low potential (150 mV vs. RHE). This could be explained by the porosity and percolation properties of FB7 series catalysts. In case of FB7-1, the abundant active sites in FB7-1 give the high current density in the vicinity of the onset potential, but its narrow mass transfer channels limit the rate of ORR in the wide voltage range. In case of FB7 and FB7-10, their linear sweeping behaviours are similar which may be due their similar mesoporous properties. However, there is not obviously proportional relationship between porosity and ORR activity, which indicates pore structure has limited contribution to ORR activity without raising the density of active sites. To further investigate the effect of structure and composition on ORR activity for Fe-N_x-C catalysts derived CTFs, two FBP7 and FP7 were prepared from 4,4'-dicyanobiphenyl and 2,6-dicyanopyridine monomers using the same synthetic procedures of catalyst FB7, respectively. The FP7 exhibits much higher nitrogen content but with a similar isotherm of type I and narrow mesoporous size distribution that of FB7-1 (Fig 4a and 4b), while the FBP7 shows lower nitrogen content

but with similar mesoporous structure of FB7. Comparing to FB7-1 and FB7, the linear sweeping behaviours in HClO₄ solution of FB7 and FBP7 can be explained well by their active sites density and pores properties (Fig. 4). In case of FBP7, it shows similar pore structure and limited current density to that of FB7, except for a much lower ORR activity. This may be due to the lower active sites density as results of the low nitrogen content in FBP7. The FP7 also exhibited much lower ORR activity than that of FB7, though the nitrogen content which are key to form highly active sites of FP7 are the highest. This may be due to the FP7 is a microporousdominated material.

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ARTICLE

To better understand the electrochemical catalytic behaviour of FB7, Tafel slope was calculated (Fig. 5a). It's obvious that the FB7 exhibits a similar Tafel slope to that of Pt/C in the low overpotential region under acidic conditions (0.1 M HClO₄), indicating that the ORR rate-determining step of this Fe-N_x-C catalyst derived CTFs may be determined by migration of adsorbed oxygen intermediates.⁴³ The H₂O₂ yield and electron transfer number (n) have also been calculated by results of RRDE test (the potential of the Pt ring electrode was set to 1.2 V vs. RHE). As shows in Fig. 5b, the H₂O₂ yield of FB7 ranges from 3.12% to 6.95% at all potential, while the electron transfer number of are relative to the 3.94 and 3.86 respectively. This demonstrates that the FB7 is capable of electrochemically catalysing the reduction of oxygen to water through four-electron-transfer process.

Meanwhile, the stability and methanol-tolerance of FB7 also has been tested in 0.1 M HClO₄. The accelerated durability test (ADT) was proceeded by RDE technique by cycling from 0.6 to 1.0 V vs. RHE at a scanning rate of 50 mV s⁻¹ under oxygen atmosphere. The FB7 exhibits excellent stability with a less 22 mV $E_{1/2}$ loss than that of Pt/C (60 mV), even after 10000 potential cycles of accelerated durability test (Fig. 5c). The methanol-tolerance test was performed by the method of current-time (I-T) plots with adding 1 M methanol to 0.1 M HClO₄ after about 300 s (at a potential of 0.667 V vs. RHE). Like most of NPCs, our FB7 clearly exhibits much better methanoltolerance ability than that of Pt/C. After 1000 seconds of currenttime (I-T) plots test, the FB7 exhibited only 11% of the relative current attenuation which is much lower than that of Pt/C (86%).

Conclusion

In summary, this work provided a simple way to prepare efficient Fe-N_x-C ORR catalysts by direct heating the dry mixture of FeBr₂, ZnCl₂ and dinitrile monomer. From the analysis of comparative samples which prepared by changing the amount of ZnCl₂ and using different dinitrile monomers, we found that mesoporous structure and the density of activity sites are the key factors to control the ORR activity of this kind catalyst. In all samples prepared herein, FB7 exhibits the most active ORR activity, which can attributable to the best balance of mesoporous structure and density of activity sites. These results may provide new ideas for designing more efficient CTFs-based ORR catalysts for PEM fuel cells.

Acknowledgements

Page 6 of 7

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The authors gratefully acknowledge the financial support of the 100-Talent Program of Chinese Academy of Sciences, the NSFC (Project Nos. 21303206), and technique support from the Prof. Xiaochun Zhou at Suzhou Institute of Nano-tech and Nanobionics, CAS.

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