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<span id="page-0-0"></span>State Key Lab of Fine Chemicals, Liaoning Key Lab for Energy Materials and Chemical Engineering, PSU-DUT Joint Center for Energy Research, Environmental and Biological Science and Technology, Dalian University of Technology, Dalian 116024, China School of Chemistry, Dalian University of Technology, Dalian 116024, China

<span id="page-0-4"></span><span id="page-0-2"></span>Key Lab of Interface Science and Engineering in Advanced Materials, Ministry of Education, Taiyuan University of Technology, Taiyuan 030024, China



<span id="page-0-3"></span> $^{\ast}$  C  $\qquad \qquad$   $\blacksquare$ E-mail addresses:  $\circledcirc$  .  $\cdot$   $\cdot$   $\circledcirc$  (J. ).<br><sup>1</sup>H.  $\cdot$  D.<sup> $\bullet$ </sup>.  $\cdot$   $\cdot$   $\cdot$  y

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 $\frac{1}{4}$  .  $\frac{10.1016}{\cdot}$  eng. 2018.12.005

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### 2. Experimental

# 2.1. Preparation of CC@ZIF-67

C  $_{\text{m}}$  (CC 2  $_{\text{m}}$  2  $_{\text{m}}$ ) y H<sub>3</sub> (69%)  $90\,C$  6  $\,$  for  $\,$  $\mathbf{r}$  to remove the remove excess according in the immersed in definition in definition of  $\mathbf{r}$  $(100 \text{ mL})$  m m C (3)<sub>2</sub>·6H<sub>2</sub> (0.72 ) m 2-m y m  $(2-M\tilde{I}_{\text{m}}, 1.64)$   $\mu$   $A$   $4$   $\mu$   $\mu$  $\mathbf{r}$  (),  $\mathbf{CC} \textcircled{a}$  IF-67  $m \rightarrow 60 \text{ C}$ 

# 2.2. Preparation of  $CC@Co_3O_4$ -PCNA and  $CC@Co_4N$ -PCNA

y y, CC@ IF-67 m 
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 7  
\n600 C 2 C<sub>mn</sub> $\eta$ <sup>-1</sup> $\eta$  m  $\eta$  2  $\eta$  2 m  
\n $\eta$  330 C 2  $\eta$ <sup>-1</sup> $\eta$  m  $\eta$  2  $\eta$  2 m  
\nCA.  
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\nC @C<sub>3</sub> 4-C A  
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\n350 C 5 C<sub>mn</sub> $\eta$   
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# 2.3. Preparation of CC@PCNA, CC@Co<sub>4</sub>N NWs, ZIF-67 and Co<sub>4</sub>N-PC

The CC@ZIF-67 was annealed in a tube furnace, heated to 600 °C at  $2 C_{m,n}^{-1}$   $2$   $2 m$   $m$   $y$   $n$ <br> $(1 M)$   $24$   $m$   $C$  $m(1 M)$   $m(24 m C)$  $CC@C$   $C$  A.  $CCC@C_3$  4  $\rightarrow$   $(CC@C_3$  4  $\rightarrow$   $\rightarrow$   $\rightarrow$   $\rightarrow$   $\rightarrow$   $\rightarrow$   $24$ .  $CC@$ using the report of the report of  $r$  and  $r$  field  $r$  and  $\begin{array}{ccc} \mathbf{C}_{3\ 4} & \longrightarrow \\ \textcolor{red}{\blacktriangleleft} & \textcolor{red}{\blacktriangleleft} & \textcolor{red}{\blacktriangleleft} & \textcolor{red}{\blacktriangleleft} & \textcolor{red}{\blacktriangleleft} & \textcolor{red}{\blacktriangleleft} & \textcolor{red}{\blacktriangleleft} \textcolor{red}{\blacktriangleleft} & \textcolor{red}{\$  $m$   $\cdot$  I<sub>n</sub> y y<sub>n</sub> , C (3)<sub>2</sub>·6H<sub>2</sub> (0.41 ), H<sub>4</sub>F (0.13 ) **a**  $(0.42)$  **b**  $(50 \text{ mL})$  were discolved into definizing  $(50 \text{ mL})$  under  $(50 \text{ mL})$  $\mathbf{u}_1 = \begin{bmatrix} 10 & \mathbf{w}_1 & \mathbf{w}_2 & \mathbf{w}_3 & \mathbf{w}_4 & \mathbf{w}_5 & \mathbf{w}_6 & \mathbf{w}_7 & \mathbf{w}_8 & \mathbf{w}_7 & \mathbf{w}_8 & \mathbf{w}_8 & \mathbf{w}_9 & \math$ immersed in the above solution for an above solution for an anomalism  $10$  min. The solution and solutio mm  $\frac{m}{c}$  were the state  $\frac{m}{c}$  m  $\frac{m}{c}$  m  $\frac{m}{c}$  m  $\frac{m}{c}$ 120  $\degree$ C  $\degree$  5  $\degree$  A down to RT, the sample was washed with water and ethanol for several  $\mathbf{r}_1$ , and  $\mathbf{r}_2$  for  $\mathbf{r}_3$  for  $\mathbf{r}_2$  for  $\mathbf{r}_3$  for  $\mathbf{r}_1$  $330 \, \text{C}$  maintained for  $\hat{\text{f}}$  in air. The final black carbon carbon carbon carbon clothes in an and  $\hat{\text{f}}$  in an analysis of  $\hat{\text{f}}$  in an analysis of  $\hat{\text{f}}$  in a carbon contract carbon carbon contract car  $m \longrightarrow \text{CC@C }_{3/4} \longrightarrow \text{CC@C }_{4} \longrightarrow$  $m \text{CC} @C_{34} \rightarrow m$  $CC@C<sub>4</sub> - C<sub>4</sub>$ 



2.4. Preparation of the sulfur composites

 $\sqrt{CC\omega}C_4 - C$  A,  $\sqrt{CC\omega}C_3$  4- C A,  $\sqrt{CC\omega}C_4$  - A<br>C A n  $\sqrt{CC}$  m y m - ff n  $\begin{array}{ccc} \sqrt{CC} & C & A & \text{m} \\ 50 & \text{m} & \text{m} \end{array}$  were prepared by  $\begin{array}{ccc} \text{m} & \text{m} & \text{m} \\ \text{m} & \text{m} & \text{m} \end{array}$ m  $50.$  To uniformly distribute  $(0.15)$  m C  $_2(10 \text{ mb})$ , D v CC@C  $_4$  -C 2 (10 mL). D y CC@C 4 - C A<br>  $\therefore$  C 20 m m. p  $\begin{array}{ccc} \mathbf{m} & \mathbf{m} & \mathbf{y} & \mathbf{m} & \mathbf{C}_2 & \mathbf{m} & \mathbf{20} \mathbf{m} & \mathbf{m} & \mathbf{m} \\ \mathbf{m} & \mathbf{50} & \mathbf{C} & \mathbf{6} & \mathbf{m} & \mathbf{CC} \otimes \mathbf{C}_4 & -\mathbf{C} & \mathbf{A} & \mathbf{m} \end{array}$  $\begin{array}{ccc} 50 \text{ C} & 6 \text{ .} & \text{ } \\ A & m & 155 \text{ C} & 12 \text{ (F . 1)} \end{array}$  (CC@)  $m = 155 \text{ C} = 12 \text{ (F. 1)}.$ C<sub>3</sub> <sub>4</sub>-CA,  $\overline{C}$ C $\otimes$ C<sub>4</sub> -  $\rightarrow$   $\overline{C}$   $\overline{C}$   $\otimes$  C  $\overline{C}$  composite  $\overline{C}$ were prepared by the same general procedure. The sulfur loading was 1.01–6.20  $\frac{y}{m}$  m<sup>-2</sup>,  $\frac{m}{n}$ 

# 2.5. Preparation of the  $Li_2S_6$  solution



# 2.6. Material characterization



#### 2.7. Electrochemical measurement



2.8. Density functional theory calculations



<span id="page-2-0"></span>

Fig. 1.  $\mathbf{m}$   $\mathbf{m$ 



 $E_b = E_{Li_2 S_n} + E_{Co_4 N} - E_{Li_2 S_n + Co_4 N}$  (1)

 $\begin{array}{ccc} \n-\mathbf{A} & E_{Li_2S_n} & \mathbf{m} & E_{Co_4N} \\
\mathbf{C}_4 & , E_{Li_2S_n+Co_4N} & \mathbf{m} & \mathbf{m} & \mathbf{y} & \mathbf{L}_{2n} - \mathbf{C}_4\n\end{array}$ ,  $E_{Li_2S_n+Coa_N}$  $\mathbf{m}$ 

# 3. Results and discussion

 $\begin{array}{ccccc} \mathbf{y}_{\mathbf{y}_{\mathbf{y}}} & \mathbf{y} & \mathbf{CC@C}_{4} - \mathbf{C} \mathbf{A} & \mathbf{y}_{\mathbf{y}} \\ \mathbf{y}_{\mathbf{y}} & \mathbf{F} & \mathbf{0} & \mathbf{F} & \mathbf{y}, \mathbf{H} \end{array}$  $\mathbf{F}$ , 1  $\mathbf{F}$ , 1 and [Fig. 1](#page-2-0) and Fig. S1. Fig.  $\mathbf{F}$ , S1. Fig. 3. Fig. 2. And was constant was obtained by the property in a H  $_{3}$  solution. The pretreated by  $_{\rm H}$ conductive CC with well-enriched oxygen-containing functional groups  $(-H, -C-H)$ seed, thus leading to strong bonding force between ZIFs and carbon cloth substrate. Then, the 2D  $IF-67$  names are grown on  $\mathbf{y}$  are grown on  $\mathbf{y}$ C (  $_{3})_{2}$ ·6H<sub>2</sub> **a**  $^{'}$  2  $\begin{array}{lll} m & y & m & (2-M \text{ Im}) & \rightarrow \\ 4 & m & \text{CC}(\text{m} \text{ IF}_2-67) & \rightarrow & y & \text{eff} \end{array}$  $CC@$  IF-67).  $\vec{P}$ - y ff  $\vec{P}$ <sup>F</sup> D) p<br>CC@ IF-67 power power diff-67  $m$  CC@ IF-67  $m$  $y \left($ Fig. 2). The successful growth of  $2 \times 10^{-11}$  growth carbon can be also confirmed by distinct confirmed by district color change from black color change from black  $y$  (F. 1).  $\mathbf{w}$ ,  $\mathbf{CC} \textcircled{a}$  IF-67  $\mathbf{f}_{\mathbf{m}}$ ,  $y$  $\mathbf{r}_1$   $\mathbf{r}_2$  CC@C<sub>4</sub> - CA<sub>pp</sub>  $\mathbf{r}_1$  $\mathbf{m}$  and  $\mathbf{m}$  and

The morphological structure of  $\mathbf{y}_m$  investigation products was investigated products w  $y$  fing  $m$  minds  $m$   $y$  (FE-EM). F  $\cdot$  2 substrate. Obviously, leaf-like nanosheets can be achieved. However, in CC, IF-67  $\frac{1}{n}$  n n n y n y  $\begin{array}{cc} \text{CC} & \text{CF}^{-7}2 \text{ m} \text{ F} & \text{2} \text{ D} \text{ FE-EM} \text{ m} \end{array}$  $CC@^TIF-67$  n n<br>  $TC@^TIF-67$  n n<br>  $TC@^TIF-67$  n n  $\mathbf{m}$  surfaces of the CF  $\cdot$  2 c). Meanwhile, the thickness of the C nnanosheets increases with time increases with time  $\mathbf{r}_n$  (Fig  $3$ ). After  $\mathbf{y}$  $\begin{array}{ccc}\nC_{3,4} & m \\
CC@C_{3,4} - C & A\n\end{array}$   $\begin{array}{ccc}\n\bullet & \bullet & \bullet & \bullet & \bullet \\
\bullet & (F \cdot 2) & \bullet & \bullet & H_3\n\end{array}$  $CC@C_3$ <sup>2</sup> 4-CA) were  $(F \cdot 2)$ . Nitridation in N<sub>H</sub><sub>3</sub> demonstrated to be an effective way for preparing specific cobalt nitride way for preparing specific cobalt ni  $24.A$ s shown in [Fig. 2](#page-2-1)erf, the surfaces of nanosheets become rough and surfaces of nanosheets become rough and surfaces become rough and surfaces of nanosheets become rough and surfaces of nanosheets become rough and surf  $\mathbf{r}_{\mathbf{n}}$  **porton**t under the increase of  $\mathbf{H}_3$  at 600 °C.  $\mathbf{m}$  can etch the case of give rise to extra space for hosting substances. It can be also seen that  $\mathbf{I}$ the carbon nanosheets reasonably become the case of  $\mathcal{S}^0$  nm) than  $\frac{\text{c} \cdot \text{c} \cdot \text{c}}{\text{c}}$ nanosheet-shaped structure and distributes on the CC surface in the relatively array form, being similar to leaves grown on branches. For  $\mathbf{r}$   $\mathbf{$  $\mathbf r$  at the following by acid etching with  $\mathbf r$ formation of porous carbon nanosheet arrays on carbon cloth (noted as  $CC\ddot{\hat{\omega}} C A, F. 4)$  and  $CC\ddot{\hat{\omega}} C A$ , Fig. 3. Second porous carbon nanosheets in  $\ddot{\omega}$  and  $\ddot{\omega}$  carbon nanosheets can be computed by  $\ddot{\omega}$  carbon nanosheets in  $\ddot{\omega}$  can be computed by  $CC$  $(C_4 - C)$  in the prepared from freely grown  $F-67$  $m \hspace{1.5cm} (F. 2).$ 

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Fig. 2. FE-EM  $_{\text{IM}}$  ( ) IF-67. (, a) CC@ IF-67. (a) CC@C<sub>3</sub> 4-PCA. (e, f) CC@C<sub>4</sub> - CA.

<span id="page-3-0"></span> $\mathbf{r}$   $\mathbf{r}$  CC@ IF-67 CC@C<sub>4</sub> - CA  $\mathbf{m} \cdot \mathbf{r} = \mathbf{m} \cdot \mathbf{m}$  transmitted by the microscope (TEM). The microscope (TEM). CC@ZIF-67 nanosheet has solid feature with lateral width of 1.5 μm  $(\mathrm{F} \;.\; 3$  ). After the conversion via oxidation via oxidation via oxidation via oxidation via oxidation and n like morphology can be well preserved by well preserved but a porous structure can be well preserved by  $\mathbf{r}$ y  $(F^{\dagger}, 3 -). F$  m magnified  $F^{\dagger}$  and  $F^{\dagger}$  and  $F^{\dagger}$ . 3d,  $\mathbf{r}$  be seen that the surface of the surface of the nanostructures is composed of many  $\mathbf{r}$ nnanoparticles with the diameters  $40$  nm embedded in the porous  $40$  nm embedded in the porous  $\sim$  $\mathbf{r}_{\mathbf{r}}$ nanostructure are shown in [Fig. 3](#page-3-0)e and Fig. 3e and Fig. 3e and Fig. 3e and Fig. S  $f(x) = 0.207$  nm n  $0.243$  nm n  $(111)$  n C 4 **a** (311) **p** C 3 4, **y**, **p** 21. **p** c  $_3$   $_4$  (space  $Fd3m$  (227)) **an** C<sub>4</sub> (Pm3m (221)) **are shown in F**  $\cdot$  5 **a**<sub>n</sub> F  $\cdot$  3, y. C<sub>4</sub> possesses a similar atomic structure with closely view  $y$ packed cobalt metal, but having  $C-C$  distance due to the N atomic state  $C$ the center of the unit cell  $\mathbf{a}$  $\overline{P}$  D  $\rightarrow$  CC, CC@C<sub>4</sub> - CA<sub>n</sub> CC@C<sub>34</sub>-CA are shown in [Fig. 4](#page-4-0). The difference peak at around 25.6° corresponds peak at around 25.6° corresponds to  $\mathbf{r}$  $(002)$  plane of  $\overline{r}$  D peaks in  $\overline{r}$ **presence**  $C_{3,4}$  (DF#42-1467) **precise of**  $\mathbf{H}_{\mathbf{p}}$  $\mathbf{r}$  a space with a space  $\mathbf{0.243}_{\mathbf{R}}$  nm, corresponding to the corresponding to the  $(311)$  $C_{3,4}$ ,  $(F.5)$ . To  $C@C<sub>4</sub> - C A$ , **Pr n** 600 °C  $-3$  h  $H_3$  fl  $50$ sccm, the nitridation temperature was optimized via control test. The  $\mathbb{P}$  D (F.6) y mp  $\mathbb{C}$  compounds at different nature. The transfer of  $C_{3,4}$   $C_{4}$  is based on the following equation is based on the following equation is  $\frac{31}{4}$ :  $24Co<sub>3</sub>O<sub>4</sub>+64NH<sub>3</sub> = 18Co<sub>4</sub>N + 23N<sub>2</sub>+96H<sub>2</sub>O$  (2)  $A$ s nitridation process, cubic cubic cubic process, cubic  $(DF#41-0943)$   $(111), (200)$   $(220)$  p  $\mathbf{c}_3$  into the transformation of  $\mathbf{c}_3$  4 in Good  $\mathbf{c}_4$  in  $\mathbf{c}_5$  $\begin{array}{cccc} \n\mathcal{P} & D & , F \ .3 & (111) & , \n\end{array}$  $\mathbf{c}$  4 mm y 0.207 nm (F.3.). As  $\sqrt{CC}$   $\ll$   $C^2$   $\ll$ 22.9, 25.7 and 27.6 and be found (Fig. 7). EM images that  $(3.5 \times 10^{-3})$  $\mathbf{r}$  matricles are distributed uniformly in porous carbon nanosheet  $\mathbf{r}$  $(F \tI)$ , suppose that support  $F$  exists we can  $G$  a - C A,

renders the composite with the possibility to act as an electrode for  $L\ B.$  and  $\mu$   $y$  induction by induct  $\mathbf{r}$ פון איך על כאשר המוצר היו ידוע למוצר המוצר היו ידוע המוצר היו ידוע היו ידוע המוצר היו ידוע היו ידוע היו י

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CC@C<sub>3</sub> <sub>4</sub>-CA, CC@C<sub>4</sub>  $-\uparrow$ <sub>n</sub>, CC@C<sub>4</sub> - CA.

Fig. 4. ( )  $\mathcal{P}$  D n CC, CC@C 3 4-C A n CC@C 4 - C A ( )  $\lim_{m \to \infty}$  CC, CC@C 4 - A n CC@C 4 - C A ( )  $\mathcal{P}$  n n

greatly enhanced. This means the promoted transformation of soluble Lips  $L_{2/2}/L_{2}$  20. Meanwhile, the Peak A1 of CC@C<sub>4</sub>-PCNA shifts to a lower potential, suggesting the activation energy is decreased, which accelerates the reaction from  $\mathbf{L}_2$  to  $\mathbf{s}$ . restrain the possibility for the shuttling of LiPSs. The distance between A1 and Peak C1 0.36  $\overrightarrow{A}$  and  $P$  case of  $\overrightarrow{AC}$  and  $P$   $\overrightarrow{C}$  case of  $\overrightarrow{C}$  and  $P$   $\overrightarrow{C}$  case of  $\overrightarrow{C}$ .  $\frac{m}{\sqrt{C}}$  /CC,  $\frac{m}{\sqrt{C}}$  9.32 V for  $\frac{C}{C}$  for  $\frac{C}{C}$  for  $\frac{C}{C}$ implies that polarization is improved because  $\mathbb{C}_4$  $\mathbf{m}^{\mathsf{T}} \longrightarrow \mathbf{m}$  in  $\mathbf{m}^{\mathsf{y}}$  with the experimental results  $\mathbf{m}$  in  $\mathbf{m}$ and previous nitrides studies  $22,34$ . peaks, and the negative shift in the anodic peaks in the S/CC@Co4N-PCNA electrode clearly reflect the catalytic activity of Co4N, which promotes the transformation of solution of solution  $L$  solution of solution  $L$  $\overline{L}$  B  $16,35,36$ . CA  $\frac{P}{P_{\text{m}}}\frac{1.7.4}{0.2}$  m,  $\frac{1.7.4}{5}$  c and  $\frac{2.8.4}{0.5}$  C and  $\frac{1.7.4}{0.5}$  c and  $\frac{1.7.4}{0.5}$  c and  $\frac{1.7.4}{0.5}$  c and  $\frac{1.7.4}{0.5}$  c and  $\frac{1}{2}$  c and  $\frac{1}{2}$  c and  $\frac{1}{2}$  c and  $\frac{1}{2}$  c  $\mathbf{m}$ , 0.2 to  $\mathbf{C}$  are shown in Fig. Section in Fig. Section in Fig. s. consist of two discharge plateaus and one charge plateau, which are in  $\begin{array}{ccc} \n\begin{array}{ccc}\n\mathbf{C} & \mathbf{C} & \mathbf{C} \\
\mathbf{C} & \mathbf{A} & \mathbf{A} \\
\mathbf{C} & \mathbf{A} & \mathbf{A}\n\end{array}\n\end{array}$  $P^{\text{max}}$  and stable with a low polarization of 170 m/ $\alpha$  and 0.5 C,  $\sqrt{CC}$  m  $\sqrt{CC}$  and  $\frac{190 \text{ m/s}}{y}$  (F. 5).  $y = \begin{bmatrix} 1 & 264 \\ 264 & 190 \\ 264 & \end{bmatrix}$  y,  $\mathbf{r}_\mathbf{n}$ y result from the fact that  $\mathbf{c}_A$  empedded into carbon nanosheets. y y<sub>m</sub> promotes the t LiPSs in charge-discharge process, as well as increasing the utilization  $\begin{array}{ccccc} \text{L} & \text{B} & 37 & \text{F} & \text{.5} \\ & \text{fi} & & / \text{CC@} \\ \end{array}$ discharge profiles of  $\int_{R_1}^{R_2}$  of  $\int_{R_1}^{R_2}$  and  $\int_{R_1}^{R_2}$  and  $\int_{R_1}^{R_2}$  and  $\int_{R_1}^{R_2}$  and  $\int_{R_2}^{R_2}$  and  $\int_{R_1}^{R_2}$  are  $\int_{R_1}^{R_2}$  and  $\int_{R_2}^{R_2}$  and  $\int_{R_1}^{R_2}$  and  $\int_{R_2}^{R$ 0.5 C with  $\begin{array}{ccc} 0.5 \text{ C} & \text{m} \\ \text{C} & \text{A} & \text{m} \end{array}$  1.7–2.8 V.  $\frac{9}{1121}$  m<sup>A</sup> <sup>-1</sup> 100 y 1455 m<sup>A</sup> y m m  $^{1121}$  m<sup>A</sup>  $^{-1}$  100 y  $I_m$ <br>m m  $^{6.20}$  m m<sup>-2</sup>, /CC@C<sub>4</sub> - C  $\mathbf{m}$  m 6.20  $\mathbf{m}^{-2}$ ,  $\sqrt{\text{CC@C}}$ <sub>4</sub> - C A  $\mathbf y$  is stable cycling performance with a slightly lower discharge  $\mathbf y$ 543 m<sup>A</sup> <sup>-1</sup> 0.5 C and  $\frac{y}{200}$  cycles (F. 10). y  $e^{45}$   $\mu$ . The important role of sulfur loading and input loading and in electrolyte/sulfur  $(E/\epsilon)$  in shape in  $L$ **unim** y in for  $\frac{38}{\cdot}$  L E/( $\mu$ L: mg): 9:1  $0.2, 0.5, 1, 2, 3, 4$  $5 \text{ C}$ ,  $\frac{1356}{9}$ ,  $\frac{1356}{9}$ , 1356, 1252, 1076, 936, 859,

802 and 746 mA  $^{-1}$  can be achieved, respectively. A  $1201 \text{ m}^{\text{A}}$ <sup>-1</sup> (88.56%) the initial parameters above  $\mathbf{y}$  recovered above  $\mathbf{y}$  recovered above  $0.2 \, \mathrm{C}$ , showing  $0.2 \, \mathrm{C$ the superior structural structural structural stability and the better conductural structural struct y  $\ln \frac{\text{CC@C A}}{\text{C@C A}}$ ,  $\text{CC@C 3 4-^C C A}$ <br>  $\text{CC@C 4}$   $\rightarrow \text{A}_\text{F}$   $\rightarrow \text{C}$  (F . 5 ). I<sub>n</sub> ,  $-\mathbf{A}_{\mathbf{N}}$   $\mathbf{C}(\mathbf{F} \cdot \mathbf{5})$ . I<sub>n</sub> fact, the high-rate capability capability of  $\mathbf{y}$  $\sqrt{CC}$ @C<sup> $\frac{W^{-1}}{4}$ </sup> C A<br>y (F. y  $(F. 11 \bullet 3)$ . And Table  $\mathbf y$  rising cobalt prices and limiting cobalt resources, lease and limiting cobalt resources, less amount of cobalt is beneficial to the decline in the price of cobalt-based batteries.  $\text{H}_{\text{H}}$  , me me me me me me me  $\int /CC\omega C_4-CA'$  and  $\mathbf{r}$  and some cobalter cobalter cathode lithium-sulfure lithium-sulfure lithium-sulfure lithium-sulfure lithium-sulfure lithium-sulfure lithium-sulfure lithium-sulfure lithium-sulfure lithium-sulfur 4)  $39,40$ .  $\mathbf{m}$  impedance spectroscopy (EIS)  $\mathbf{m}$  measurements of fresh cells were conducted to explore their electrochemical dynamics. R is the impedance contributed by the impedance contributed by the resistance of the resistance of the  $\mathbf y$  , Represents the charge transfer represents the charge transfer resistance between the charge tra electrolyte and sulfur electrode, R is the deposit diffusion resistance of SEI film, and CPE arises from double-layer capacitance. Obviously, S/  $CC@C<sub>4</sub> - C<sub>4</sub>$  $m \rightarrow$   $m$  (F  $\cdot$  12). Moreover, the wettable wettability and we the wettability and we the wettability and we the wettability and we the wellconductivity are also important for in electrode materials  $\mathbf{r}$  $\begin{array}{ccc}41.A \quad \text{m } \mathbb{F} & . & 13, \end{array}$  a shown in contact angle from 120° to 11°, is attributed to the fact that the grown nanosheet array can be grown nanosheet arrays can be  $\mathbf y$  improve the hydrophilicity of the carbon cloth surface  $\mathbf y$  and  $\mathbf y$  and  $\mathbf y$  and  $\mathbf z$ . F  $(F - 14)$  show that the conductivity of CC@C<sub>3</sub> 4- C A C A  $(2.59 \t10^3 \t m^{-1})$  is higher than the CC@C  $_3$  4- C A  $(1.85 \t10^3 \t m^{-1})$  is  $\cdot$  H  $_3$ - CC  $(1.53 \t10^3 \t m^{-1})$ . I  $(H_{3} - \overrightarrow{CC}$  (1.53  $10^{3} \text{ m}^{-1}$ ). I favorable for the fast transport of  $\mathbf y$ the active materials, the effective unit unit unit utilization of  $\mathbb{I}$ the electromagnetic material. As  $\mathbf{M} = \mathbf{M} + \mathbf{M} +$  $\begin{array}{ccc} \text{C} & \text{A} & \text{A} & \text{B} & \text{C} & \text{A} \end{array}$ **a b**  $0.1 \text{ C}$ ,  $\text{/CC@C}_4 - \text{ C}$  A  $y = 727 \text{ m}^{\text{A}}$  and the discharge capacity is defined and the discharge capacity is defined as  $y = 1$  $500 \text{ mA}$   $^{-1}$  100 y . A 500 y ,  $\text{/CC@}$  $C_4 - C A$  maintains a discharge capacity of  $598 \text{ m}^\text{A}$ <sup>-1</sup>. campan is  $\frac{y}{x}$  or  $\frac{y}{m}$  is  $\frac{y}{m}$  on  $\frac{y}{m}$  if  $\frac{y}{m}$ 

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Fig. 5. (a) Cyclic voltammograms curves, (b) Galvanostatic discharge and charge curves of S/CC, S/CC@Co3 4-PCNA and S/CC@Co4N-PCNA at 0.5 C. (c) cycle performance at 0.5 C, (d)  $y(\mathbf{r}_m, \mathbf{r}_m, 0.2 \text{ C} - 5 \text{ C})$  /CC, /CC@C<sub>3</sub> 4-CA, /CC@C<sub>4</sub> -A<sub>n</sub> /CC@CCA<sub>n</sub> /CC@C4-CA. (e) L<sub>n</sub> -  $\mathbf{r}_m, \mathbf{y}_m, \mathbf{r}_m, \mathbf{r}_m$  $\texttt{C}_4-\texttt{C}$  A high current at a high current density of  $\texttt{C}_4-\texttt{C}$  and after a function of  $\texttt{C}_4-\texttt{C}$  and a function  $\texttt{C}_4-\texttt{C}$  and a function  $\texttt{C}_5$ 

 $\frac{100\%}{3D}$  in charge-discharge-discharge-discharge-discharge-discharge process. The leaf-like morphology and  $\frac{100\%}{3D}$  in charge- $3D$  braintain well after the cycling and  $y$  as shown by the cycling as show digital photon, FE-EM  $\frac{m}{R}$ ,  $\frac{m}{R}$ ,  $\frac{m}{15}$ ,  $\frac{m}{R}$ ,  $\frac{m}{R}$  $\begin{array}{ccc} \mathbf{F} & \mathbf{5} & \mathbf{F} & \mathbf{15} \end{array}$ , which function  $CC@C_4 - C A$ .  $\begin{array}{cc}\n\mathbf{y} & \text{/CC@C } 4 \cdot \text{C A} \\
\text{ff} & \text{N} & \text{I} & \text{N} & \text{N} \\
\end{array}$ on restriction of the diffusion of LiPSs, density function of  $\mathbf{L}$  is denoted by  $\mathbf{y}$ calculations were performed to examine the interaction between sulfur  $S_{\rm H}$ , C<sub>4</sub> (F. 6, F. 16-17). (111)  $S_{\rm H}$  C<sub>4</sub> chosen as the representative crystalline planes for the simulations owing to their least surface energy and most stable structure. The binding energy between Co4N nanocrystals and S8, Li2 8, Li2 6, Li2 4,  $L_{2,2}$ ,  $L_{2}$ ,  $L_{2}$   $-5.33, -7.22, -4.21, -4.18, -6.01$  and  $-4.66$ . respectively. This indicates that the interaction between the polysulfide  $\mathbf{s}_m \cdot \mathbf{C}_4$  is much stronger than that between  $\mathbf{C}_3$  4 and Lipsse  $\mathbf y = 43,44$ , and also superior to those of other polarization to those of other polarization of other polariz m  $22,45-47$ . DF  $\rightarrow$  m  $\rightarrow$  These DF  $\begin{array}{ccc} \n\mathbf{r}_1 \cdot \mathbf{r}_2 & \mathbf{r}_2 \cdot \mathbf{r}_3 & \mathbf{r}_3 \cdot \mathbf{r}_4 & \mathbf{r}_5 \cdot \mathbf{r}_5 & \mathbf{r}_6 \cdot \mathbf{r}_4 & \mathbf{r}_5 \cdot \mathbf{r}_5 & \mathbf{r}_6 \cdot \mathbf{r}_6 & \mathbf{r}_7 \cdot \mathbf{r}_7 & \mathbf{r}_8 \cdot \mathbf{r}_8 & \mathbf{r}_9 \cdot \mathbf{r}_9 & \mathbf{r}_9 \cdot \mathbf{r}_9 & \mathbf{r}_9 \cdot \mathbf{r}_9 & \mathbf{r}_9$  $\mathbf{C}_4$  L.  $\mathbf{y}$  fi adsorption abilities of different materials were experimentally and  $\mathbb{F}_{p}$ v<sub>in</sub>, as  $\mathbf{y} = \mathbf{y}$ ,  $\mathbf{y} = \mathbf{y}$ , the L<sub>2</sub> 6 ff  $\mathbf{y}$ 

y solution becomes more transparent after the addition  $\mathbf{C}$ 

 $C_4 - C_A$  m tion capability among these materials. The XPS analysis of CC@Co4N- $\begin{array}{ccc} \text{C} \text{A} & \text{m} & \text{L}_{2 \text{6}} & \text{m} & \text{m} \text{m} \end{array}$ formed to provide additional evidence for the strong interaction  $\bullet$  between Lipschips and Lipschips and Lipschips and Lipschips  $L$ 1  $\frac{C_0C_4 + L_2}{0.7}$  shows a strong peak at  $\frac{1}{2}$  s separate peak at  $0.7$  eV shift towards lower binding energy compared with the  $y$  compared with the  $y$  compared with the  $y$ L-<br>  $L = \frac{1}{2} \int_{0.}^{\frac{\pi}{2}} \frac{L}{56.4 \times 1} \frac{56.3 \times 1}{1} \frac{K}{1}$  reported in previous literature in previous literature in previous literature in previous literature in provided in provided in provided in provided in prov  $\tt L$ -<sub>M</sub> 56.4 eV <sub>m</sub> L<sub>M</sub>  $\tt L$ <sub>m</sub>  $\tt m$ <sub>m</sub> C<sub>4</sub>  $\begin{array}{ccccccc}\nL^2 & \mathbf{m} & 30.4 & \mathbf{m} & \mathbf{m} & \mathbf{m} & \mathbf{m} & \mathbf{m} \\
57. \mathbf{M} & \mathbf{m} & , & \mathbf{P} & \mathbf{C} & 2 & & \mathbf{C}\mathbf{C}\mathbf{C} & 4 & -\mathbf{C} & \mathbf{A} \\
\mathbf{m} & \mathbf{F} & . & 19 & , & \mathbf{m} & & & \\
\mathbf{m} & & & & & & \\
\mathbf$  $\mathbf{F}$  in  $\mathbf{F}$  in  $\mathbf{C}$  2  $\mathbf{F}$  in  $\mathbf{C}$  2  $\mathbf{F}$  and  $\mathbf{C}$  2  $\mathbf{F}$  are  $\mathbf{C}$  are  $\mathbf{C}$  are  $\mathbf{C}$  are  $\mathbf{C}$  are  $\mathbf{C}$  are  $\mathbf{C}$  are  $\mathbf{F}$  $C$  2<sub>1/2</sub> and C<sub>4</sub>.  $\blacksquare$ and  $\mu$  solution, both peaks shift about 1.0 and 1.1 eV toward lower binding energy and the intensity of th 778.5 eV decreases [\[29\].](#page-8-2) Based on these facts, it can be reasonably  $c_4$  have a strong chemical affine  $\mathfrak{m}$  affine  $\mathfrak{m}$  $\lim_{n\to\infty}$  in the results are also in good agreement with the results are also in good  $m \text{DF}$ .  $T \rightarrow$   $/CC@C<sub>4</sub> - C<sub>A</sub>$ electron is assumed to the strong interaction between  $\mathbb{L}$  and  $\mathbb{L}$  and  $\mathbb{L}$ as its facilitate electron in transportation and in the  $\frac{1}{2}$ 

reaction at  $\mathbb{C}^d$  measurements were conducted at different were conducted at different at different at different at different at  $\mathbb{C}^d$  measurements were conducted at different at different at different at differe

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Fig. 6. (a) Calculated interaction energy (E ) of Li2 (x = 1, 2, 4, 6 or 8) species and S8 on the (111) planes of Co4N crystals. (b) Representative voltammograms of S/CC@Co4N-PCNA cathode obtained at different scan rates. (c) Peak currents versus square root of scan rates of S/CC, S/CC@Co3 4-PCNA and S/CC@Co4N-PCNA. (d) Li<sup>+</sup> diffusion coefficient comparison (1) C  $\frac{1}{P}$ ,  $\frac{1}{P}$ ,  $\frac{1}{P}$ ,  $\frac{1}{P}$ ,  $\frac{1}{P}$ <br>
(CC,  $\frac{1}{\sqrt{C}}$  /CC@C<sub>3 4</sub>-C A  $\frac{1}{P}$  /CC@C<sub>4</sub> - C A





<span id="page-7-14"></span>

# <span id="page-7-3"></span>4. Conclusions



# <span id="page-7-13"></span>Acknowledgment

<span id="page-7-12"></span><span id="page-7-4"></span> $Y$ matural Natural Natural Science  $Y$ matural Natural Natural Science  $F$ C<sub>n</sub> (G<sub>n</sub> .51672033, 1610105, 1610255),  $\mathbb{F}_n$  $KyL$  y  $I_m$  nabineering  $KyL$  $\begin{array}{ccccccc}\n & K y & L & & y & I_m & & \eta & E_m & m & m & A \\
M & , M & y & E & & m & (KLI EAM 201601), & & \\
m & m & F & m & & L & & E & m & m\n\end{array}$ Open Sharing Fund Projects for Large Equipment Testing, Dalian  $-\frac{1}{6}$  y  $\frac{1}{7}$  y, C<sub>m</sub> (2016-54).

# <span id="page-7-5"></span>Appendix A. Supporting information

<span id="page-7-8"></span><span id="page-7-7"></span><span id="page-7-6"></span>
$$
m \neq \frac{y}{2}
$$
 :10.1016/ .  $m \neq m$  :2018.12.005

## References

<span id="page-7-11"></span><span id="page-7-10"></span><span id="page-7-9"></span><span id="page-7-2"></span><span id="page-7-1"></span><span id="page-7-0"></span>1. G.B , .A.F , , L.J.H , J.M.  
\n2. 
$$
-\frac{1}{\sqrt{2}}
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,  $\frac{1}{\sqrt{2}}$ ,

mm 9 (2017) 29881–29888.<br>
26 M.S. Balogun, C. Huang, A. H. Mater. H.B. J.,  $\vec{r}$ . Balogundates on the theory of the theor

- <span id="page-8-0"></span>[development of nanostructured transition metal nitrides for electrochemical energy](http://refhub.elsevier.com/S2405-8297(18)31118-8/sbref26) [storage and water splitting, Mater. Today 20 \(2017\) 425](http://refhub.elsevier.com/S2405-8297(18)31118-8/sbref26)–451.
- <span id="page-8-1"></span> $[27 \ldots \ldots]$ <sub>m</sub>, K.  $\tilde{r}$ ,  $\ldots$ <sub>m</sub>,  $\tilde{r}$ . L. L<sub>i</sub>,  $\ldots$ ,  $\ldots$   $\mathcal{N}$ <sub>m</sub>,  $\ldots$ <sub>n</sub>, C.<sub>Z</sub>.  $\ldots$ <sub>b</sub> [Cobalt nitrides as a class of metallic electrocatalysts for the oxygen evolution](http://refhub.elsevier.com/S2405-8297(18)31118-8/sbref27) of the oxygen evolution of the oxygen evoluti
- 28 L.B.  $\frac{1}{\sqrt{7}}, \frac{1}{\sqrt{7}}, \frac$
- <span id="page-8-2"></span>
- <span id="page-8-8"></span>[29] [D.R. Deng, F. Xue, Y.J. Jia, J.C. Ye, C.D. Bai, M.S. Zheng, Q.F. Dong, Co4](http://refhub.elsevier.com/S2405-8297(18)31118-8/sbref29) [nanosheet assembled mesoporous sphere as a matrix for ultrahigh sulfur content](http://refhub.elsevier.com/S2405-8297(18)31118-8/sbref29) [lithium-sulfur batteries, ACS Nano 11 \(2017\) 6031](http://refhub.elsevier.com/S2405-8297(18)31118-8/sbref29)–6039. [30] [K.R. Yoon, K. Shin, J. Park, S.H. Cho, C. Kim, J.W. Jung, J.Y. Cheong, H.R. Byon,](http://refhub.elsevier.com/S2405-8297(18)31118-8/sbref30) [H.M. Lee, I.D. Kim, Brush-like cobalt nitride anchored carbon nano](http://refhub.elsevier.com/S2405-8297(18)31118-8/sbref30)fiber mem-
- <span id="page-8-9"></span>
- 
- 
- [brane: current collector-catalyst integrated cathode for long cycle Li-O2](http://refhub.elsevier.com/S2405-8297(18)31118-8/sbref30) batteries, [ACS Nano 12 \(2018\) 128](http://refhub.elsevier.com/S2405-8297(18)31118-8/sbref30)–139. [31] [M.D. Meganathan, S. Mao, T.Z. Huang, G.X. Sun, Reduced graphene oxide](http://refhub.elsevier.com/S2405-8297(18)31118-8/sbref31) [intercalated Co2C or Co4N nanoparticles as an e](http://refhub.elsevier.com/S2405-8297(18)31118-8/sbref31)fficient and durable fuel cell catalyst [for oxygen reduction, J. Mater. Chem. A 5 \(2017\) 2972](http://refhub.elsevier.com/S2405-8297(18)31118-8/sbref31)–2980. [32] [X. Li, Q. Sun, J. Liu, B. Xiao, R. Li, X. Sun, Tunable porous structure of metal](http://refhub.elsevier.com/S2405-8297(18)31118-8/sbref32) [organic framework derived carbon and the application in lithium](http://refhub.elsevier.com/S2405-8297(18)31118-8/sbref32)–sulfur batteries, [J. Power Sources 302 \(2016\) 174](http://refhub.elsevier.com/S2405-8297(18)31118-8/sbref32)–179. [33] [W. Guo, C. Yu, S. Li, J. Yang, Z. Liu, C. Zhao, H. Huang, M. Zhang, X. Han, Y. Niu,](http://refhub.elsevier.com/S2405-8297(18)31118-8/sbref33) [J. Qiu, High-stacking-density, superior-roughness LDH bridged with vertically](http://refhub.elsevier.com/S2405-8297(18)31118-8/sbref33) [aligned graphene for high-performance asymmetric supercapacitors, Small 13](http://refhub.elsevier.com/S2405-8297(18)31118-8/sbref33) [\(2017\) 1701288.](http://refhub.elsevier.com/S2405-8297(18)31118-8/sbref33) [34] [T. Zhou, W. Lv, J. Li, G. Zhou, Y. Zhao, S. Fan, B. Liu, B. Li, F. Kang, Q.-H. Yang,](http://refhub.elsevier.com/S2405-8297(18)31118-8/sbref34)
- $\frac{m}{m} = \frac{m}{y} = \frac{m}{m} = \frac{m$
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- <span id="page-8-10"></span>36 C. L,  $\overline{r}$ ,  $\$
- <span id="page-8-11"></span>
- <span id="page-8-12"></span> $\frac{m}{262}$  (2014) 380–385.
- **40** M. H y , M.  $^{262}$  (2014) 380-360.

of pure lithium cobalt oxide films by electron resonance sputtering,  $\lim_{n \to \infty} y$  electron resonance sputtering, J.

- <span id="page-8-13"></span>41 B.  $y_m$ ,  $y_m$ ,  $-\frac{1}{2}m$ ,  $y_m$ ,  $\frac{1}{2}M \cdot F_m$ ,  $\ldots$ ,  $m$ <br>  $\frac{m}{2}$ ,  $\frac$
- <span id="page-8-14"></span>42 . L,  $\frac{m}{2}$ , J,  $\frac{1}{2}$ ,  $\frac{m}{2}$ ,  $\frac{1}{2}$ ,  $\frac{m}{2}$ ,  $\frac{1}{2}$ ,  $\frac{m}{2}$ ,  $\frac{1}{2}$ ,
- <span id="page-8-15"></span>
- ${\bf r}$ , J. M. C.  ${\bf r}$ , A 6 (2018) 2797–2807.<br>
44 L.,  ${\bf A}$ C<sub>n</sub>, J. H<sub>uan</sub>, C. <sub>w</sub>, H. <sub>m</sub>, C.  ${\bf A}$ <sub>m</sub>,  ${\bf A}$ <sub>m</sub>, L, J. X<sup>io</sup>m<sub>n</sub>,
- $M = m \rightarrow y$ <br>  $m^{2}$ <br>  $m^{$
- 
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- 7274–[7283.](http://refhub.elsevier.com/S2405-8297(18)31118-8/sbref45)<br>
46 .  $\frac{1}{n}$ , D.K.  $\frac{1}{n}$ , L.F.  $\frac{1}{n}$ , A.  $\frac{1}{n}$ , T.  $\frac{1}{n}$ , 3 (2016) 130–136.<br>
47 . L, J.  $\frac{1}{n}$ , B. G.  $\frac{1}{n}$ , D.  $\frac{1}{n}$ , L.M. L.,  $\overrightarrow{T}$ ,  $\frac{1}{n}$ , A.<br>
48 . L,  $\overrightarrow{T}$ ,  $\overrightarrow{T}$ ,  $\$
- 
- <span id="page-8-18"></span>[batteries, Small 13 \(2017\) 1701013.](http://refhub.elsevier.com/S2405-8297(18)31118-8/sbref48) [49] [X. Tao, J. Wang, C. Liu, H. Wang, H. Yao, G. Zheng, Z.W. Seh, Q. Cai, W. Li,](http://refhub.elsevier.com/S2405-8297(18)31118-8/sbref49) [G. Zhou, C. Zu, Y. Cui, Balancing surface adsorption and di](http://refhub.elsevier.com/S2405-8297(18)31118-8/sbref49)ffusion of lithium-polysulfi[des on nonconductive oxides for lithium-sulfur battery design, Nat.](http://refhub.elsevier.com/S2405-8297(18)31118-8/sbref49)
- <span id="page-8-4"></span>
- <span id="page-8-3"></span> $\begin{array}{lllllllllll} & \mathbb{C} & \mathbf{m}\mathbf{m} & \mathbf{m} & 7 & (2016) & 11203. \\[2mm] \mathbf{50} & \mathbf{\mathcal{T}}^5, \mathbf{J}, \mathbf{K}^5, \mathbf{L} & \mathbf{L} \mathbf{E}, & \mathbf{A} & \mathbf{y} & \mathbf{m}^7 \\[2mm] \mathbf{51} & \mathbf{G}, \mathbf{K} & \mathbf{J}, \mathbf{H} & \mathbf{m}^7 & \mathbf{m} & \mathbf{y} & \mathbf{M}^7 \\[2mm] \mathbf{y} & \$
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- <span id="page-8-5"></span>
- <span id="page-8-7"></span>
- <span id="page-8-16"></span>
- <span id="page-8-17"></span>
- <span id="page-8-6"></span>[54] [J.P. Perdew, Y. Wang, Accurate and simple analytic representation of the electron-](http://refhub.elsevier.com/S2405-8297(18)31118-8/sbref54)[gas correlation energy, Phys. Rev. B 45 \(1992\) 13244](http://refhub.elsevier.com/S2405-8297(18)31118-8/sbref54)–13249. [55] [H.J. Monkhorst, J.D. Pack, Special points for brillouin-zone integrations, Phys.](http://refhub.elsevier.com/S2405-8297(18)31118-8/sbref55) [Rev. B 13 \(1976\) 5188](http://refhub.elsevier.com/S2405-8297(18)31118-8/sbref55)–5192. [56] [G. Zhou, H. Tian, Y. Jin, X. Tao, B. Liu, R. Zhang, Z.W. Seh, D. Zhuo, Y. Liu, J. Sun,](http://refhub.elsevier.com/S2405-8297(18)31118-8/sbref56) [J. Zhao, C. Zu, D.S. Wu, Q. Zhang, Y. Cui, Catalytic oxidation of Li2S on the surface](http://refhub.elsevier.com/S2405-8297(18)31118-8/sbref56) of metal sulfi[des for Li-S batteries, Proc. Natl. Acad. Sci. USA 114 \(2017\) 840](http://refhub.elsevier.com/S2405-8297(18)31118-8/sbref56)–845. [57] [J. Xu, W. Zhang, H. Fan, F. Cheng, D. Su, G. Wang, Promoting lithium polysul](http://refhub.elsevier.com/S2405-8297(18)31118-8/sbref57)fide/ sulfi[de redox kinetics by the catalyzing of zinc sul](http://refhub.elsevier.com/S2405-8297(18)31118-8/sbref57)fide for high performance lithium-[sulfur battery, Nano Energy 51 \(2018\) 73](http://refhub.elsevier.com/S2405-8297(18)31118-8/sbref57)–82.