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A high-energy potassium-sulfur battery enabled by facile and effective imidazole-solvated copper catalysts

Nien-Chu Lai, Guangtao Cong and Yi-Chun Lu*

Electrochemical Energy and Interfaces Laboratory, Department of Mechanical and Automation Engineering, The Chinese University of Hong Kong, N.T. 999077, Hong Kong SAR, China

E-mail: yichunlu@mae.cuhk.edu.hk

Experimental Section

Materials. 1, 2-Dimethoxyethane (DME, Aldrich), Dimethylsulfoxide (DMSO, Aldrich) and Diglyme (DG, Aldrich) were dried over activated molecular sieves (4 Å, Aldrich) for at least one month before use. 1-methylimidazole (Me-Im) and potassium metal (K), which was stored in mineral oil were received from Sigma-Aldrich and stored in an Ar-filled glove box (Etelux, <1.0 ppm of H_2O and <1.0 ppm of O_2). The water contents of all solvents were determined by Karl Fischer titration (TitroLine 7500 KF, SI Analytics, Germany) to be less than 10 ppm. Carbon paper (AvCarb MGL190, Av Carb Material Solutions), quartz fiber filter (QMA, Whatman), potassium trifluoromethanesulfonate (KTFS, Aldrich) and copper (II) trifluoromethanesulfonate ($Cu(TFS)_2$, TCI) were dried under dynamic vacuum at 120 °C for 24 h in a glass oven (Büchi, Switzerland) and transferred to the glove box without exposure to the ambient atmosphere. Sulfur (S_8, Aldrich), *N*-methyl-2-pyrrolidone (NMP, Aldrich), polyvinylidene fluoride (PVDF, Aldrich), Vulcan carbon (VC, Cabot Co., USA), Super P carbon black powder (Super P, MTI Co.), Biphenyl (Bp, Aldrich) and potassium beta-alumina disk (K-β"-Al_2O_3, Ionotec Ltd, ϕ 20 mm, 1 mm thickness) were used as received.

Cathode preparation. The bulk sulfur electrode was prepared by employing S_8/VC composite: Super P: PVDF = 80:10:10 in NMP and drop-cast onto carbon paper (ϕ 12 mm x (0.1 ± 0.01) mm). The S_8/VC composite was made by mixing S_8:VC = 7:3 and sonicating in DME for 30 min, then it was dried at 155 °C overnight for the infiltration of liquid sulfur into the pores of VC. The sulfur electrodes were dried under 60 °C overnight to remove water and NMP. The average area weight loading of sulfur materials was about 1-1.2 mg cm^{-2}. Various electrolytes for cathode were prepared: 0.35 M KTFS in Me-Im, 0.3 M $Cu(TFS)_2$-0.1 M KTFS in Me-Im and 0.25 M $Cu(TFS)_2$-0.1 M KTFS in DG or DMSO.

Liquid anode preparation. 1.0 M BpK in DME solution was prepared by dissolving equivalent K metal into 1.0 M biphenyl DME solution according to the procedure described in the literature.[1]

Cell assembly. The anode of the BpK-S cell was constructed by subsequently placing one piece of nickel foam disk (ϕ 16 mm, 2 mm thickness) and one piece of quartz fiber (ϕ 16 mm) into one anode cap of LIR2030 coin cell followed by the addition of 0.3 mL of as-made 1.0 M BpK in DME solution. A two-compartment cell configuration as reported previously was adopted for all cells in this work, in which a polymer-laminated K-β''-Al_2O_3 was adopted to separate the cathode from the anode.[2] The cathodes for BpK-S cells were comprised of one piece of carbon papers (ϕ 12 mm) with the bulk sulfur electrode stacked on top of two pieces of blank carbon paper (ϕ 12 mm), which was impregnated with 40 μL of 0.35 M KTFS in Me-Im. For the BpK-S cell with Cu-containing homogeneous catalyst, the electrolyte for cathode was replaced with calculated amount of 0.3 M $Cu(TFS)_2$-0.1 M KTFS in Me-Im and the cell was designated as BpK-S/Cu^{2+}. The control group, BpK-Cu^{2+} cell was assembled following the above procedures and impregnating with the same amount of 0.3 M $Cu(TFS)_2$-0.1 M KTFS in Me-Im except for the use of blank carbon papers. The amount of 0.3 M $Cu(TFS)_2$-0.1 M KTFS Me-Im electrolyte for the BpK-S/Cu^{2+} cell was calculated to fix the sulfur-to-copper ratio to 3 in this work.

Electrochemical measurement. Cyclic voltammetry (CV) tests were performed at 0.1 mV s^{-1} using the two-compartment cell configuration and the anode was used as reference electrode for the CV scans. All electrochemical measurements including CV, electrochemical impedance spectroscopy and galvanostatic cycling characterizations were conducted using a VMP3 electrochemical testing unit (Bio-Logic).

Characterizations. Cells after electrochemical tests were dissembled in the glove box. The discharged/charged carbon paper cathodes were taken out of the cell, gently rinsed in 0.5 mL dry DME and then dried under vacuum at room temperature before characterizations. X-ray diffraction (XRD) measurements were conducted on a Rigaku SmartLab diffractometer (Cu Kα radiation) at a scan rate of 1 degree min^{-1}. Raman analysis was performed using a Micro Raman spectrometer (RM-1000, Renishaw Co. Ltd.). The samples were sealed on the top of slide glass with a Kapton tape in the glove box. X-ray photoelectron spectroscopy (XPS) spectra in this work was performed by using a multi-technique ultra-high vacuum Imaging XPS Microprobe system (Thermo VG Scientific ESCALab 250). Data were collected with pass energy of 20 eV for the core-shell spectra, with the takeoff angle fixed at 0 degree. For non-conductive samples, non-monochromatic Al Kα X-ray source from twin anode was used. The sample was transported to the XPS chamber under Ar, and transferred into chamber very quickly to prevent air contamination.

Density functional theory (DFT) calculations. DFT calculations were carried out with the Gaussian 16 software. All the geometries of the molecules have been fully optimized at the B3LYP/3-21G level in gaseous phase. Starting models were based on the crystal structures.

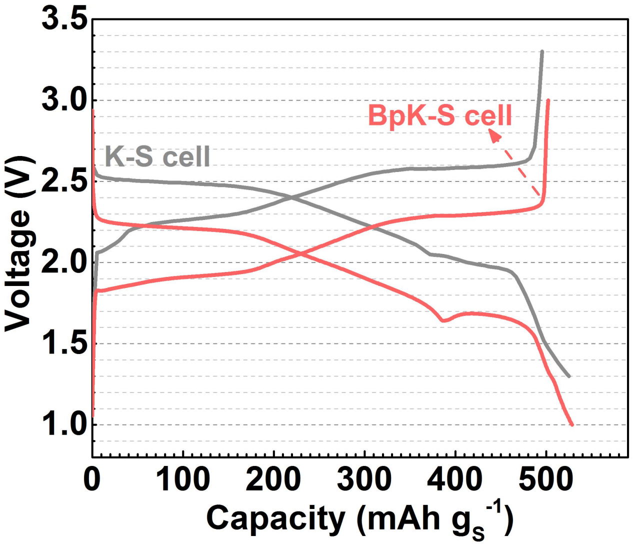

Fig. S1 Galvanostatic voltage profiles of K-S (gray) and BpK-S (red) cells at a current density of 300 mA g_S^{-1} with the cut-off voltages of 1.3-3.3 V_K and 1.0-3.0 V_{BPK}, respectively.

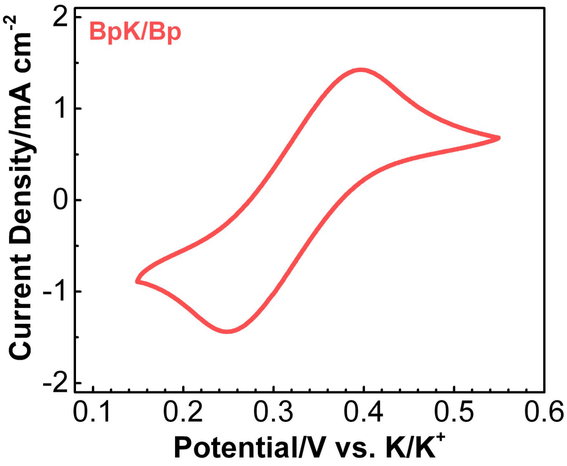

Fig. S2 CV of 10 mM BpK complex anode in DME at 250 mV s^{-1}.

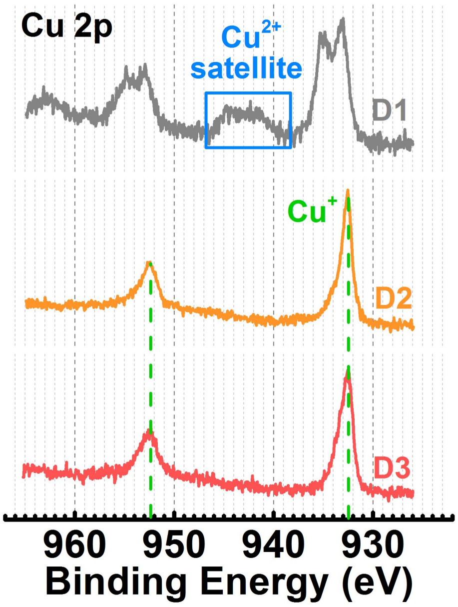

Fig. S3 The Cu 2p XPS spectra of the cathodes at various stages that are marked in Figure 3b from the BpK-S/Cu^{2+} cell. The galvanostatic test at 265 μA cm^{-2} with cut-off voltage of 1.0 V_{BPK}.

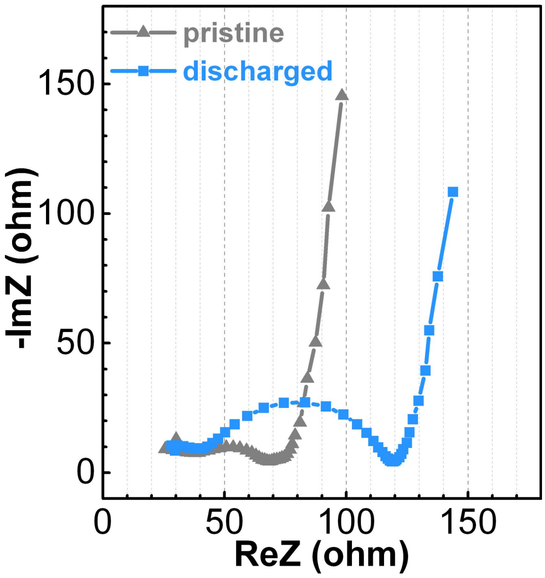

Fig. S4 Electrochemical impedance spectra collected from pure S cell before and after the first discharge.

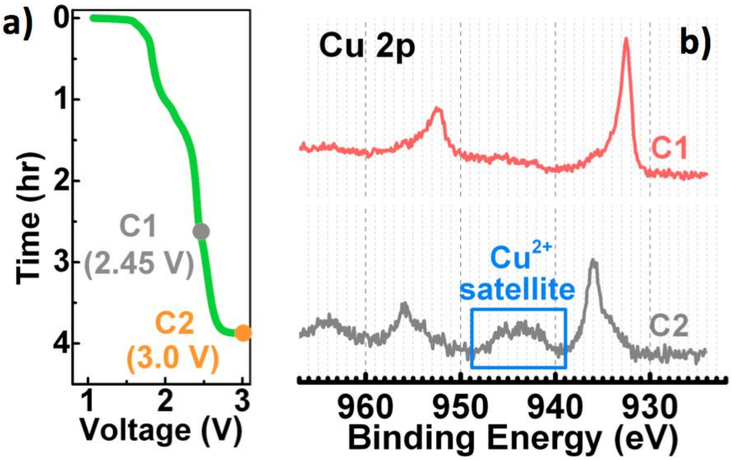

Fig. S5 a) The charge curve at 265 μA cm^{-2} and b) the Cu 2p XPS spectra of electrodes collected at charging step of C1 and C2 from the BpK-S/Cu^{2+} cell.

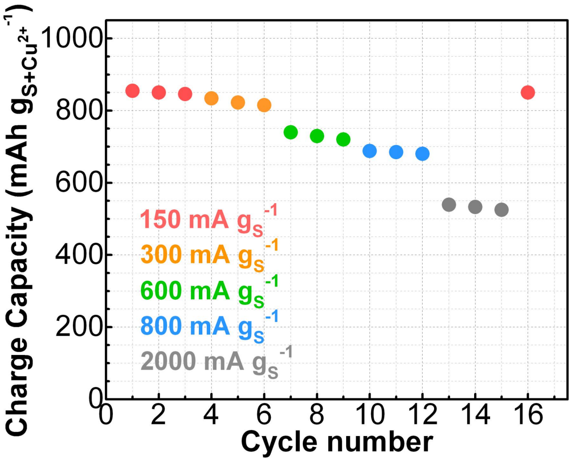

Fig. S6 Rate capability from 0.09 C to 1.2 C with cut-off voltage of 1.0-3.0 V_{BPK} for the BpK- S/Cu^{2+} cell.

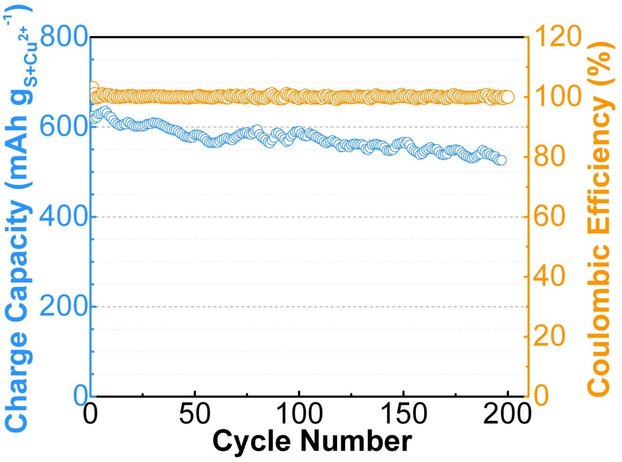

Fig. S7 The charge capacity and Coulombic efficiency as a function of cycle number at 0.48 C for the BpK-S/Cu^{2+} cell.

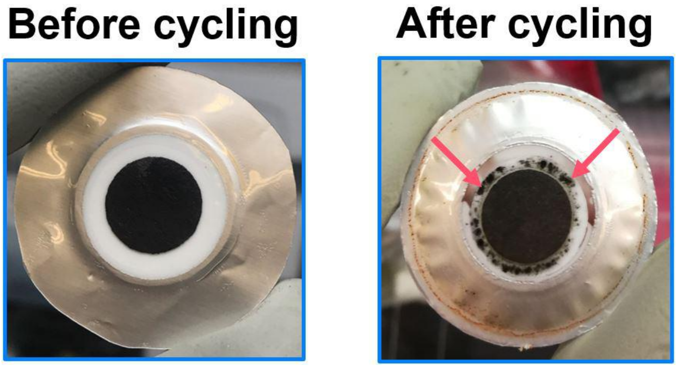

Fig. S8 Top view of digital photographs of the polymer-laminated K-β''-Al_2O_3 on the cathode side before and after stability test.

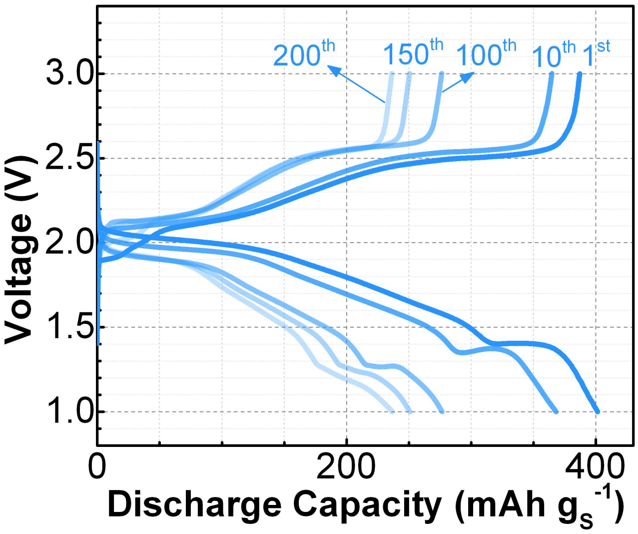

Fig. S9 The selected galvanostatic discharge and charge curves for BpK-S cell at 0.48 C for the first 200th cycles.

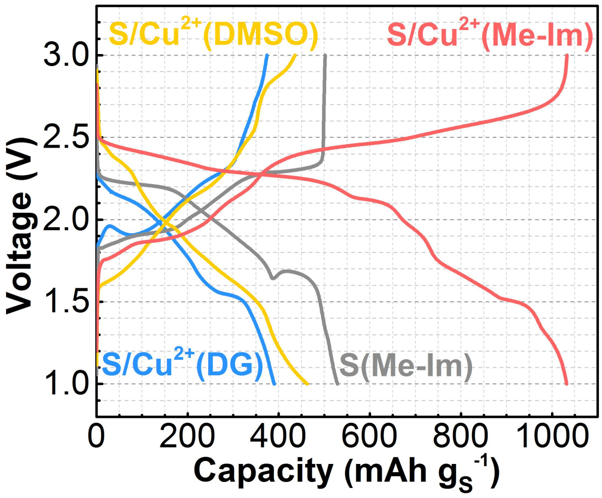

Fig. S10 The galvanostatic voltage profiles from BpK-S cell (grey) and BpK-S/Cu^{2+} cells using DG (blue), DMSO (yellow) and Me-Im (red) as the cathode electrolyte, respectively. The galvanostatic tests at 600 mA g_S^{-1}.

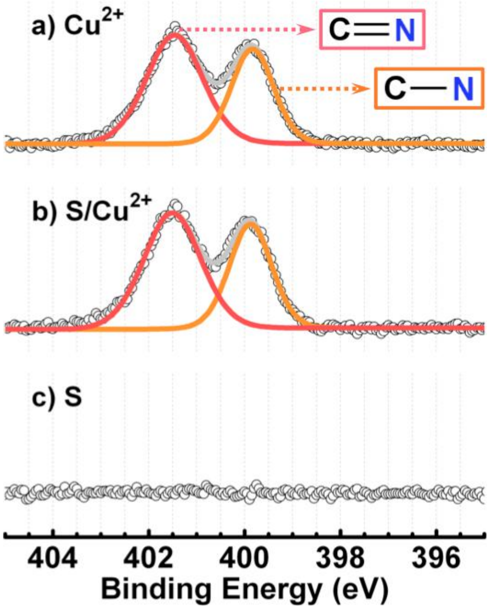

Fig. S11 The N 1s XPS spectra of the pristine cathodes from the a) BpK-Cu^{2+} cell, b) BpK-S/Cu^{2+} cell and c) BpK-S cell.

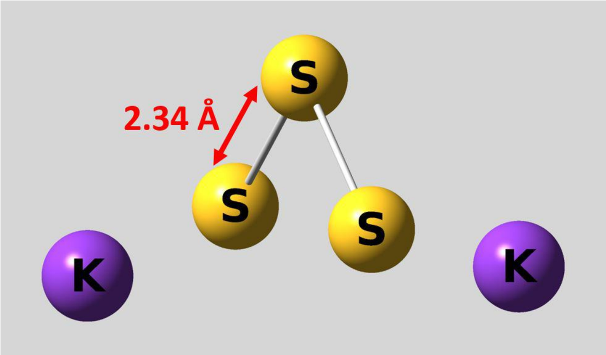

Fig. S12 The optimized geometry of K_2S_3 molecule at B3LYP/3-21G level.

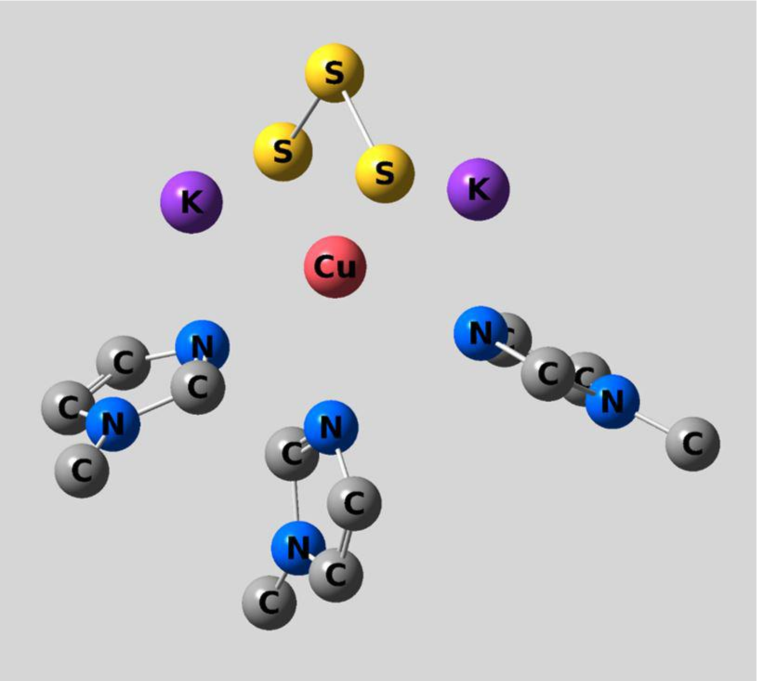

Fig. S13 The constructed geometry of the model copper catalyst with coordination by Me-Im nitrogen and polysulfide sulfur. Hydrogen atoms are omitted for clarity.

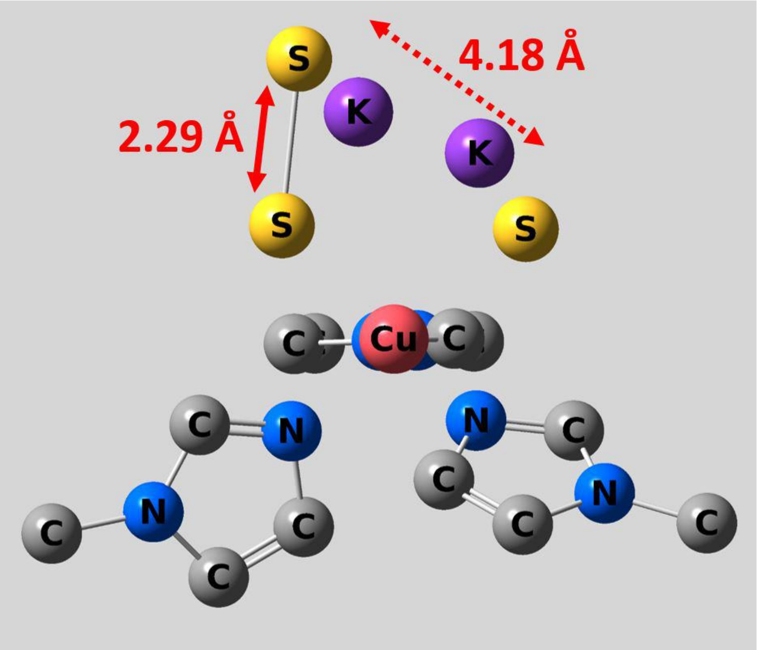

Fig. S14 The optimized geometry of the copper catalyst with coordination by Me-Im nitrogen and polysulfide sulfur at B3LYP/3-21G level. Hydrogen atoms are omitted for clarity.

Table S1 Comparison of electrochemical conditions and energy density with reported K-S batteries.

	Discharge capacity	Average cell voltage	Energy density[a]	Current density
	mAh g_s^{-1}	V	Wh Kg_s^{-1}	mA g_s^{-1}
Hwang et al.[3]	235	1.2	282	55.8
Zhao et al.[4]	528	1.06	559	50
Liu et al.[5]	710	1.28	908	328
Gu et al.[6]	520	1.95	1014	50
Ma et al.[7]	873	1.3	1135	255
Hwang et al.[8]	1050	1.1	1155	838
Xiong et al.[9]	1198	1.03	1234	20
This work	922	1.93	1779	300

[a] The energy density values E (Wh Kg_s^{-1}) were calculated as: E =Cd*Vd, where Cd represents for the practical discharge capacity, Vd represents for the average cell voltage.[7,8]

References:

(1) Cong, G.; Wang, W.; Lai, N.-C.; Liang, Z.; Lu, Y.-C. *Nature Materials* **2019**, *18*, 390.

(2) Metzger, M.; Marino, C.; Sicklinger, J.; Haering, D.; Gasteiger, H. A. *Journal of The Electrochemical Society* **2015**, *162*, A1123.

(3) Hwang, J.-Y.; Kim, H. M.; Yoon, C. S.; Sun, Y.-K. *ACS Energy Letters* **2018**, *3*, 540.

(4) Zhao, Q.; Hu, Y.; Zhang, K.; Chen, J. *Inorganic Chemistry* **2014**, *53*, 9000.

(5) Liu, Y.; Wang, W.; Wang, J.; Zhang, Y.; Zhu, Y.; Chen, Y.; Fu, L.; Wu, Y. *Chemical Communications* **2018**, *54*, 2288.

(6) Gu, S.; Xiao, N.; Wu, F.; Bai, Y.; Wu, C.; Wu, Y. *ACS Energy Letters* **2018**, *3*, 2858.

(7) Ma, R.; Fan, L.; Wang, J.; Lu, B. *Electrochimica Acta* **2019**, *293*, 191.

(8) Hwang, J.-Y.; Kim, H. M.; Sun, Y.-K. *Journal of Materials Chemistry A* **2018**, *6*, 14587.

(9) Xiong, P.; Han, X.; Zhao, X.; Bai, P.; Liu, Y.; Sun, J.; Xu, Y. *ACS Nano* **2019**, *13*, 2536.