Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information:

Bi-doped Carbon Dots for Stable Lithium Metal Anode

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Experimental Section

Preparation of Bi-CDs

The Bi-CDs were obtained by one-step hydrothermal method. Specifically, 0.55 g glucose monohydrate ($C_6H_{12}O_6 \cdot H_2O$) and 0.57 g bismuth potassium citrate ($C_{12}H_{10}BiKO_{14}$) were dissolved in 60 mL deionized water under constant ultrasound, and then the mixture was transferred into a 100 mL Teflon lined stainless steel autoclave and heated at 160 °C for 12 h. After that, the reaction solution was cooled down to the room temperature naturally, the obtained product was centrifuged for 5 min at the speed of 10000 rpm until the large size particles to be removed. Then, the Bi-CDs purification was further performed by dialyzing in a dialysis bag for 3 days, followed by freeze-dried to obtain brown powder (Bi-CDs).

Preparation of sulfur cathode

The sulfur-carbon cathode was prepared according to previous report[1]. Next, cathode plate was acquired by mixing 80 wt% the pre-prepared sulfur-carbon composites, 10 wt% binder polyvinylidene fluoride (PVDF), and 10 wt% conductive carbon (Super P) in N-methyl pyrrolidinone (NMP). The well-mixed slurry was coated onto Al foil and further dried under vacuum at 60 °C for 12 h. The diameters of cathode, separator, and anode in a full cell are 14mm, 19mm, 16mm, respectively. The areal mass loading of the active material was ~1.0 mg cm^{-2}. 80 μL of electrolyte was supplied in each cell.

Materials characterization

The microstructural and surface state of Bi-CDs were characterized by typical transmission electron microscopy (TEM) (JEM-2100F), X-ray diffraction (XRD) (Rigaku Ultima IV), X-ray photoelectron spectroscopy (XPS) (Thermo Scientific Escalab 250Xi) and Fourier transform infrared spectroscopy (FTIR) (AVTA-TAR, 370), respectively. The morphology of Li^+ ions deposition with and without Bi-CDs added were characterized by scanning transmission electron microscopy (SEM) (JEOL JSM-7610 F Plus). In detail, the coin cells after different cycles were

disassembled in the Ar-filled glove box and then the electrodes were rinsed to remove the residual electrolyte solute by 1,2-dimethoxyethane (DME) and 1,3-dioxolane (DOL) before observation.

Electrochemical measurements

In an Ar-filled glove box (O_2<0.01 ppm, H_2O<0.01 ppm), the Bi-CDs powders were dispersed into conventional electrolyte (1.0 M LiTFSI+2.0 wt% $LiNO_3$ in DME:DOL=1:1). All of the electrochemical performance tests were carried out at room temperature and using standard CR2016-type coin cells on battery testing system (LAND, Wuhan, China). The Li|Cu half-cells were assembled with lithium foil anode as well as copper foil cathode for coulombic efficiency testing and then the Li|Cu half-cells were cycled within a voltage range of 0 to 1.0 V (vs. Li^+/Li) at current densities of 0.5 and 1.0 mA cm^{-2}. As for long-term cycling, the Li|Li symmetric-cells were assembled with two lithium foils and then tested at the current densities at 0.5, 1.0, 2.0, 3.0 and 5.0 mA cm^{-2} with an areal capacity of 1.0 mAh cm^{-2}. Besides, Li-S full-cells were assembled with as-prepared sulfur cathode and lithium anode and were tested within a voltage range of 1.7 to 2.8 V (vs. Li^+/Li) at rate of 0.2, 0.5, 1.0 and 2.0 C (1.0 C=1675 mAh g^{-1}). Moreover, the electrochemical impedance spectroscopy (EIS) was tested on Solartron 1260 and 1287 with a frequency range from 10^{-1} to 10^5 Hz with the amplitude of 5.0 mV.

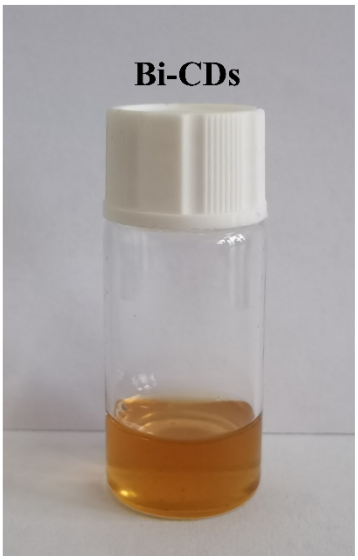

Figure S1. Digital photo of the conventional electrolyte with Bi-CDs.

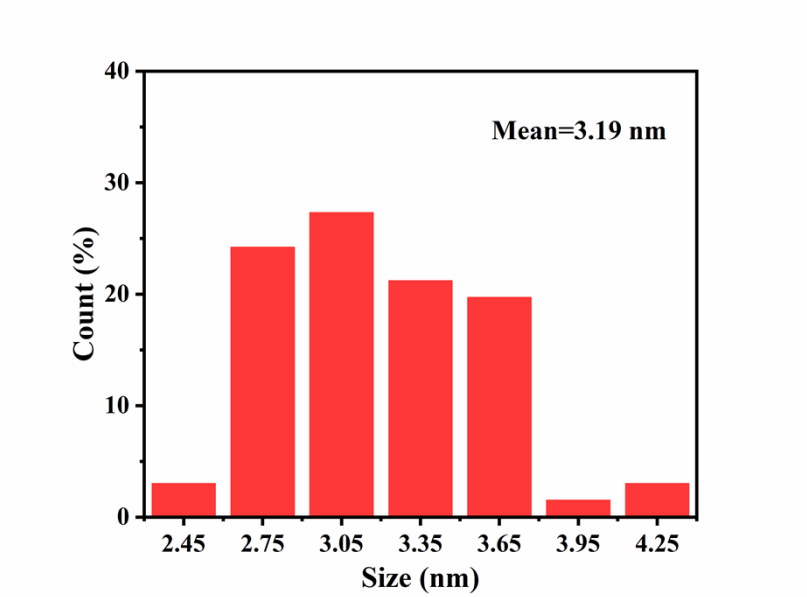

Figure S2. The size distribution of Bi-CDs.

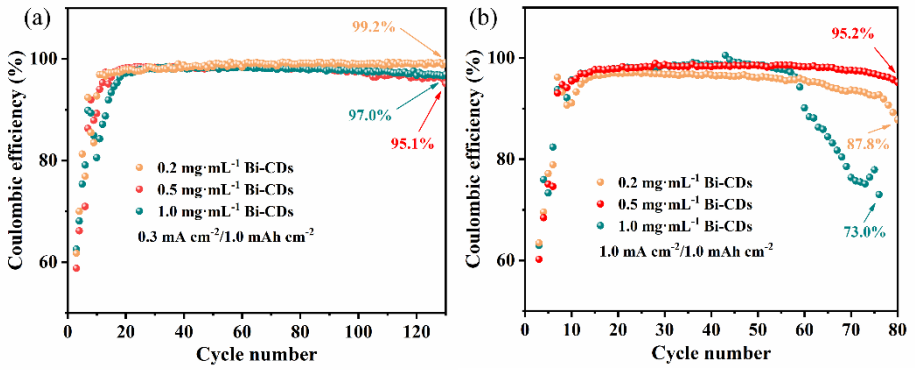

Figure S3. The Coulombic efficiency of Li|Cu half-cells with different concentration of the Bi-CDs additives at 0.3 mA cm^{-2} (a) and 1.0 mA cm^{-2} (b) with a capacity of 1.0 mAh cm^{-2}.

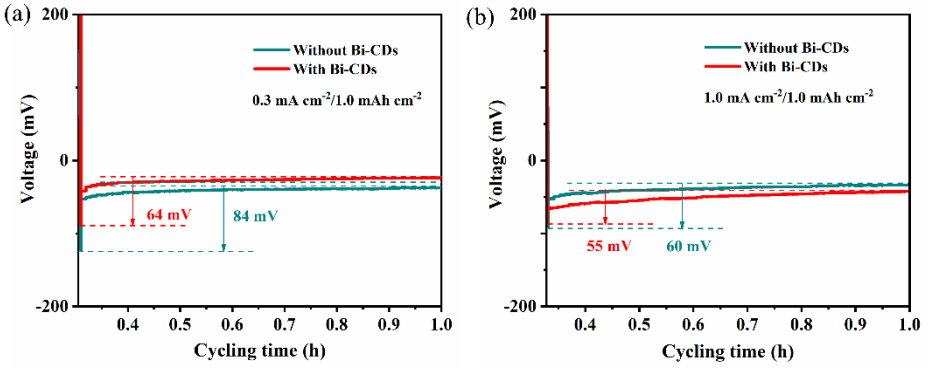

Figure S4. The initial circle overpotential of Li|Cu hall-cells with and without Bi-CDs at (a) 0.3 mA cm^{-2} and (b) 1.0 mA cm^{-2} with an areal capacity of 1.0 mAh cm^{-2}.

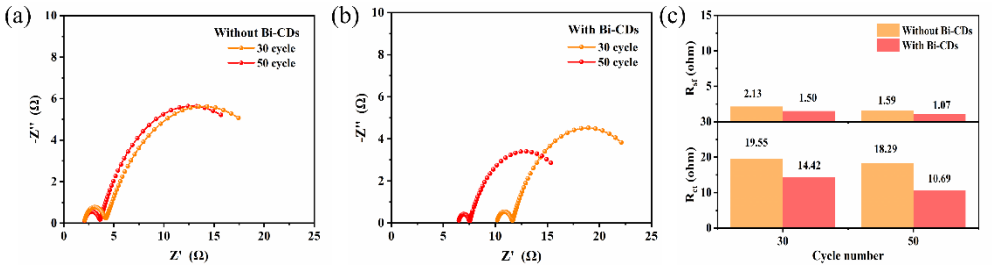

Figure S5. The Nyquist plots of Li|Li symmetric-cell with (a) and without Bi-CDs additives (b) at different cycles with their corresponding charge transfer resistance (c).

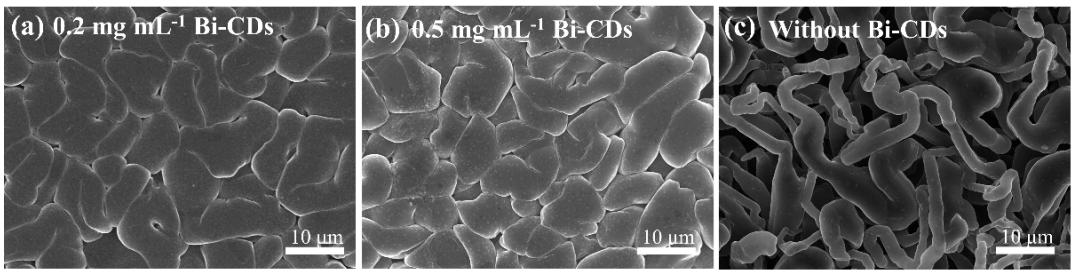

Figure S6. SEM images of the lithium ions deposition on the copper foil with Bi-CDs (a, b) and (c) without Bi-CDs at a current density of 5.0 mA cm^{-2} and areal capacity of 1.0 mAh cm^{-2}.

Notes and references

1. F. Qin, X. Wang, K. Zhang, J. Fang, J. Li and Y. Lai, *Nano Energy*, 2017, **38**, 137-146.