Supporting Information

The exploration and analysis of superfluous lithium storage capacity of Bi_2Se_3-based composite

Zidong He,[a] Zhenglei Geng,[a] Yujie Huang,[a] Xue Zhong,[a] Yujin Li,[a] Siyang Gan,[a] Meiqing Guo,[b] Wentao Deng,[a] Guoqiang Zou,[a] Hongshuai Hou*[a] and Xiaobo Ji[a]*

[a] *College of Chemistry and Chemical Engineering, National Energy Metal Resources and New Materials Key Laboratory, State Key Laboratory of Powder Metallurgy, Central South University, Changsha, 410083, China*

[b] *College of Aeronautics and Astronautics, Taiyuan University of Technology, Taiyuan ,030024, China*

Corresponding Author

** E-mail: hs-hou@csu.edu.cn (H. Hou), guomeiqing@tyut.edu.cn (M.Guo)*

Experimental section

Synthesis of CDs: All the chemicals and reagents were analytical grade and used without purification. The synthesis of CDs was conducted through the Kilogram-scale preparation of carbon dots (kCDs) process described in our previous report.[1]

Synthesis of Bi_2Se_3-CDs-Ni: The preparation of Bi_2Se_3-CDs-Ni composites was mainly carried out by solvothermal reaction. Generally, 0.8 g $Bi(NO_3)_3 \cdot 5H_2O$ (≥ 98.0%, obtained from Aladdin) and 0.4 g Na_2SeO_3 (obtained from Aladdin) were added into 60 ml glycol (obtained from Macklin) and stirred to obtain a uniform solution. Then, another solution (0.6 mmol $Ni(NO_3)_2 \cdot 6H_2O$ dissolved in 30 ml glycol) was further added to the above solution, and 0.1 g CDs was added after it was evenly mixed, and continued to stir for 5-10 minutes. The resulting solution was transferred to a 150 ml Teflon-lined stainless-steel autoclave high-pressure reactor and reacted at 200 °C for 12 h. After cooling to room temperature, the collected products are filtered, washed repeatedly with deionized water and ethanol, and finally dried in a vacuum oven. As a contrast, Bi_2Se_3-Ni and Bi_2Se_3-CDs composites can be prepared without adding CDs or $Ni(NO_3)_2 \cdot 6H_2O$ in the above process, respectively.

Materials characterization: XRD (Rigaku Model ULTIMA IV, CuKα radiation) was employed to investigate the physical phase of Bi_2Se_3-CDs-Ni, Bi_2Se_3-CD and Bi_2Se_3-Ni. Raman spectra were measured by using Raman spectroscopy (Renishaw) with a 532 nm laser excitation. Electron paramagnetic resonance (EPR) spectra were measured on Bruker EMXplus-6/1 at room temperature. The surface chemical states of the samples were investigated utilizing XPS measured by Thermo Scientific K-Alpha. The microstructure of Bi_2Se_3-CDs-Ni, Bi_2Se_3-CD and Bi_2Se_3-Ni were characterized by using scanning electron microscopy (SEM, ZEISS Sigma 300) and transmission electron microscopy (TEM, JEOL JEM-F200). Atomic force microscopy (AFM) measurements were carried out on Bruker Dimension Icon.

Electrochemical measurements: The lithium storage performances of Bi_2Se_3-CDs-Ni, Bi_2Se_3-CD and Bi_2Se_3-Ni were investigated by using CR2016 coin cell. The electrodes were composed of active materials, acetylene black (super P), and carboxymethyl cellulose (CMC) with a mass ratio of 70:15:15. The uniform slurry was coated on carbon-containing Cu foil current collector and dried at 80 °C for 12 h in a vacuum. The lithium metal was used as the counter electrode and poly propylene film (Celgard 2400) as the separator. The electrolyte consists of a solution of 1.0 M $LiFP_6$ in ethylene carbonate (EC): dimethyl carbonate (DMC): diethyl carbonate (DEC) in a volume ratio of 1:1:1 with 5.0% fluoroethylene carbonate (FEC).

And CR2016 coin cells were assembled in an argon filled glove box (both H_2O and $O_2 < 0.5$ ppm). Galvanostatic charge/discharge tests were conducted by LAND CT2001A, the galvanostatic intermittent titration technique (GITT) testing was also measured using this testing system. Cyclic voltammetry (CV) profiles were tested via MULTI AUTO LAB M204. The voltage range of all tests above were 0.01-3.00 V (vs. Li^+/Li).

Ex/in-situ analysis: For *ex-situ* XPS testing, several lithium half-cells were discharged to different states using the LAND CT-2001A instrument at a current density of 1.0 A g^{-1}. The cycled cells were transferred to an argon filled glove box for disassembly and were washed with dimethyl carbonate (DMC) until the electrolyte was washed off. The structure of the cycled material was then analysed by XPS (Thermo Scientific K-Alpha). Further *in-situ* XRD testing was carried out in continuous scan mode using a XRD instrument (Rigaku Model ULTIMA IV, CuKα radiation). It was assembled in an argon filled glove box. During the continuous scanning of the sample, the *in-situ* XRD cell was simultaneously discharged using the LAND battery test system.

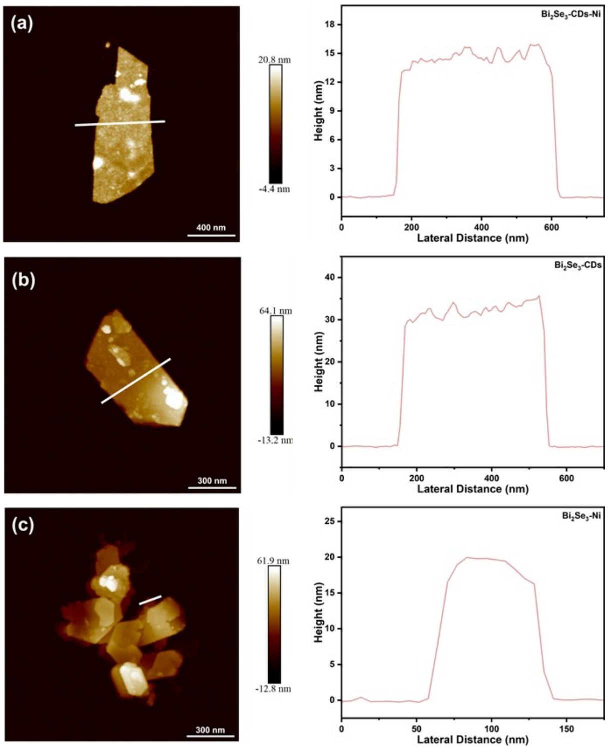

Figure S1. AFM images of a) Bi_2Se_3-CDs-Ni, b) Bi_2Se_3-CDs, c) Bi_2Se_3-Ni.

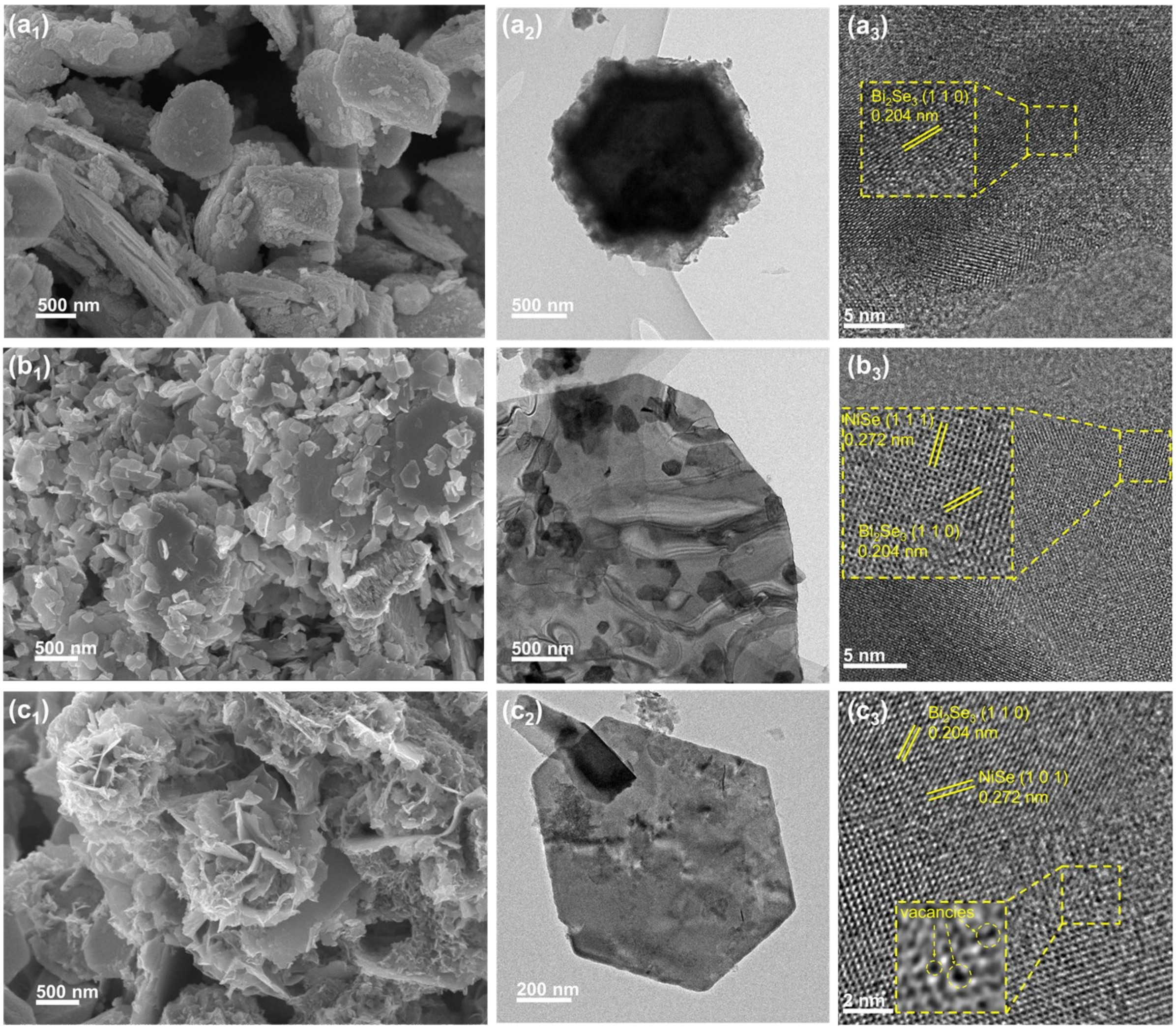

Figure S2. SEM, TEM and HRTEM images of a_1-a_3) Bi_2Se_3-CDs, b_1-b_3) Bi_2Se_3-Ni, c_1-c_3) Bi_2Se_3-CDs-Ni.

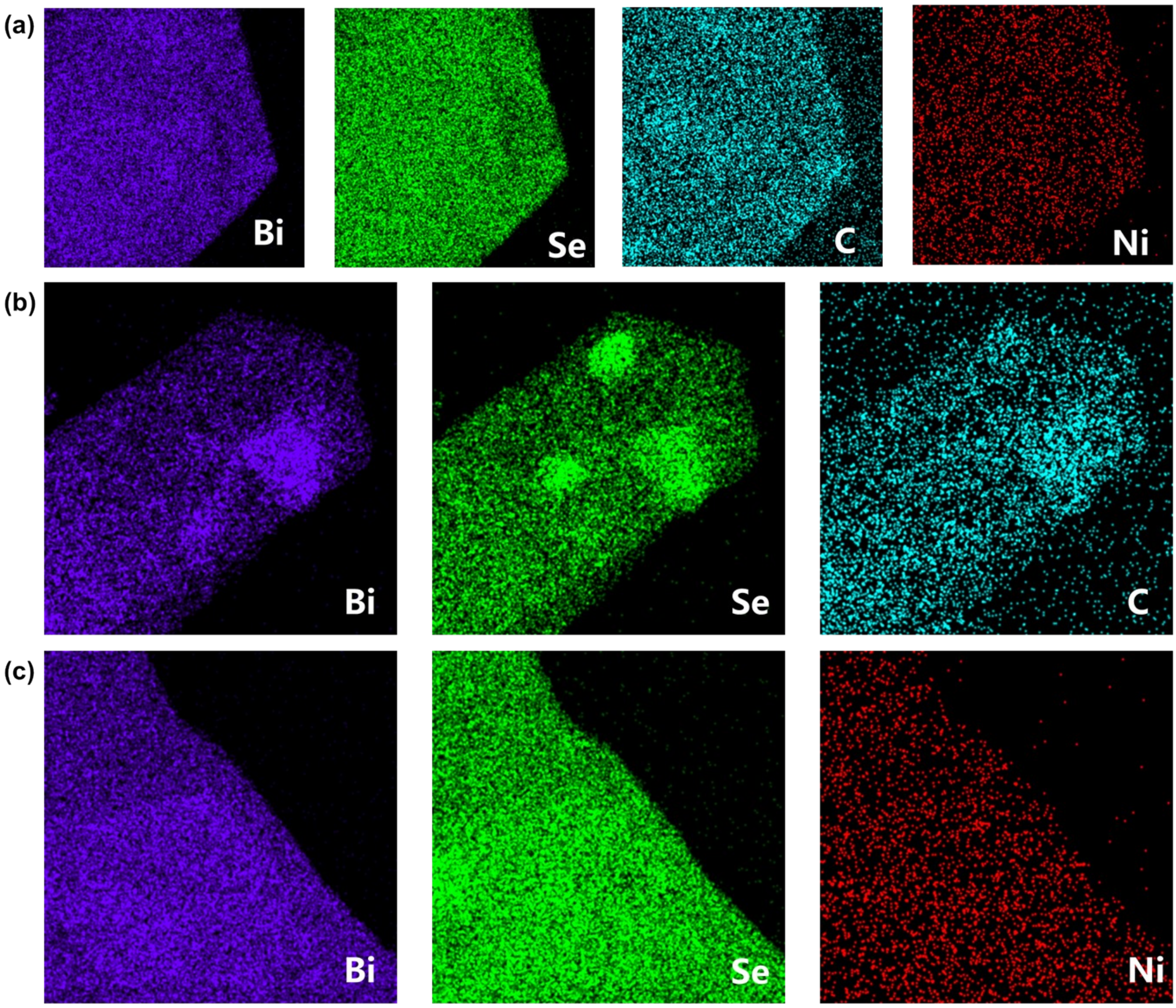

Figure S3. EDX element mapping images of a) Bi_2Se_3-CDs-Ni, b) Bi_2Se_3-CDs, c) Bi_2Se_3-Ni.

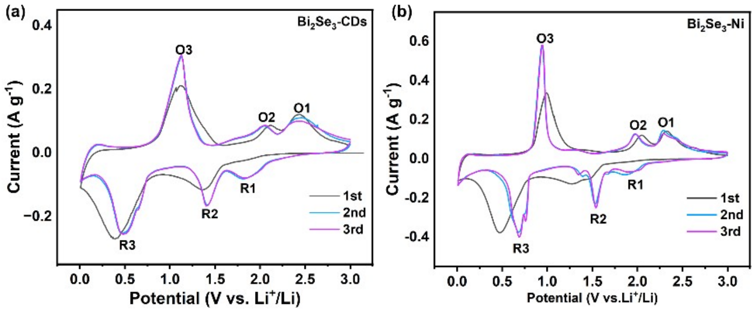

Figure S4. CV curves of a) Bi_2Se_3-CDs, b) Bi_2Se_3-Ni at a scan rate of 0.1 mV s^{-1}.

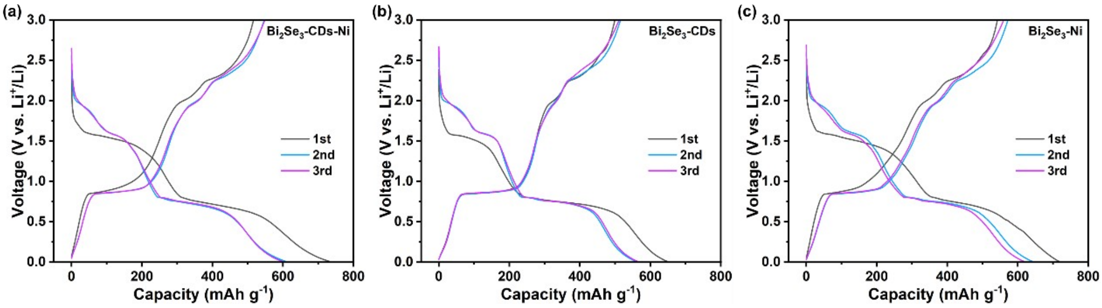

Figure S5. Charge/discharge profiles for the initial three cycles at a scan rate of 0.1 mV s^{-1} within 0.01-3.0 V of a) Bi_2Se_3-CDs-Ni, b) Bi_2Se_3-CDs, c) Bi_2Se_3-Ni.

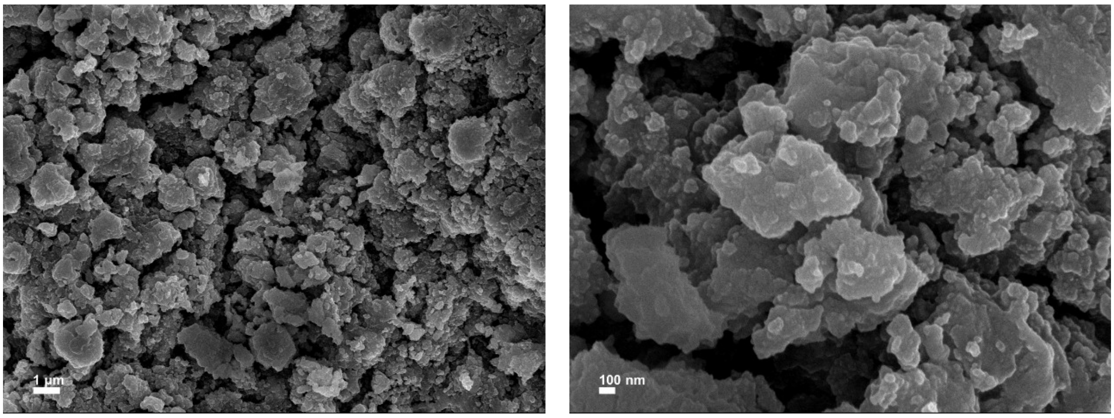

Figure S6. SEM images of Bi_2Se_3-CDs-Ni electrode after 200 cycles at 1 A g^{-1}.

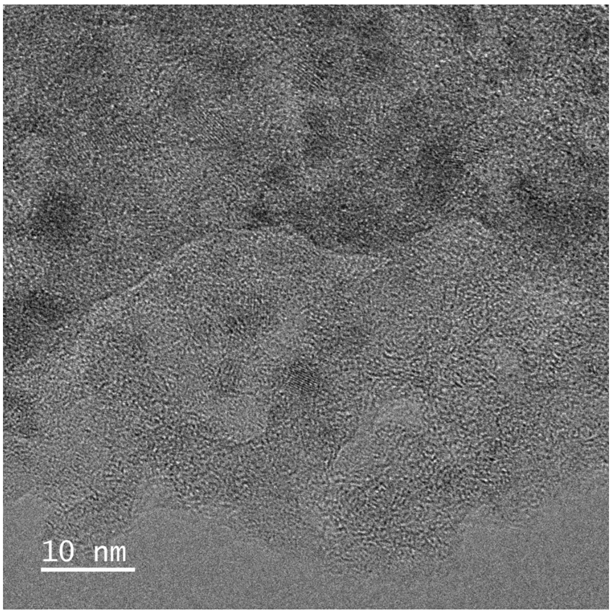

Figure S7. TEM images of Bi_2Se_3-CDs-Ni electrode after 750 cycles at 1 A g^{-1}.

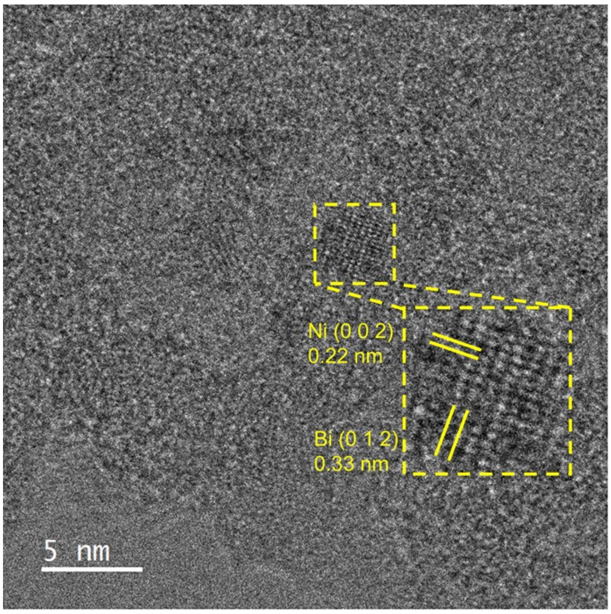

Figure S8. HRTEM images of Bi_2Se_3-CDs-Ni electrode after 750 cycles at 1 A g^{-1}.

Table S1. The data of inductively coupled plasma atomic emission spectrometry (ICP-AES)

Samples	**Mass Concentration of Bi (mg/L)**	**Mass Concentration of Ni (mg/L)**	**Atomic Ratio of Bi to Ni**
Bi_2Se_3-CDs-Ni	**14.98**	**0.907**	**4.64:1**
Bi_2Se_3-Ni	**16.53**	**1.336**	**3.48:1**

Table S2. The comparison of various Bi_2Se_3-based materials reported in the literature.

Active material	**Reversible capacity [mA h g^{-1}] / rate**	**Maximum rate capacity [mA h g^{-1}] /rate**	**Refs.**
Bi_2Se_3-CDs-Ni	942, 0.1 A g^{-1}	275, 5 A g^{-1}	This work
Bi_2Se_3@C	637, 0.2 A g^{-1}	304, 2 A g^{-1}	2
Bi_2Se_3@NC	400, 0.5 A g^{-1}	380, 1 A g^{-1}	3
Bi_2Se_3/Graphene	203, 0.05 A g^{-1}	30, 1 A g^{-1}	4
MCYS Bi_2Se_3@C	392.2, 0.2 A g^{-1}	301.5, 2 A g^{-1}	5
Bi_2Se_3/CNFs	443, 0.1 A g^{-1}	159, 4 A g^{-1}	6
Bi_2Se_3@C	469, 0.1 A g-1	93, 5 A g^{-1}	7
Bi_2Se_3@NC–400	410.6, 0.1 A g-1	572.9, 1 A g^{-1}	8
hexagonal Bi_2Se_3	99.1, 0.1 A g^{-1}	114, 1 A g^{-1}	9

Reference

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