

## Supporting Information

### **Enhancing the Li<sup>+</sup> storage capability of transition metal sulfides by *in-situ* regulating the phase conversion in operating batteries**

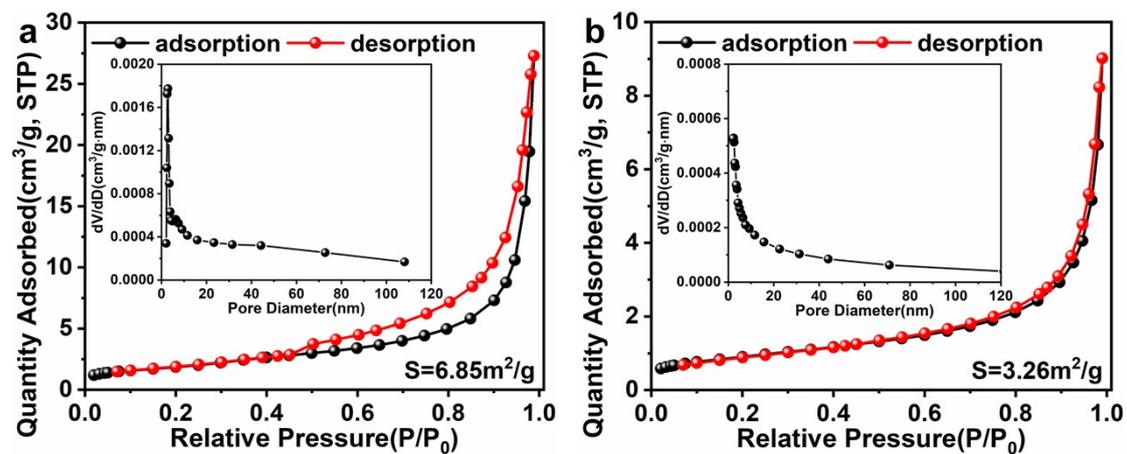
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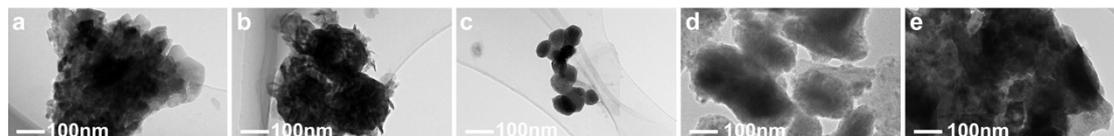
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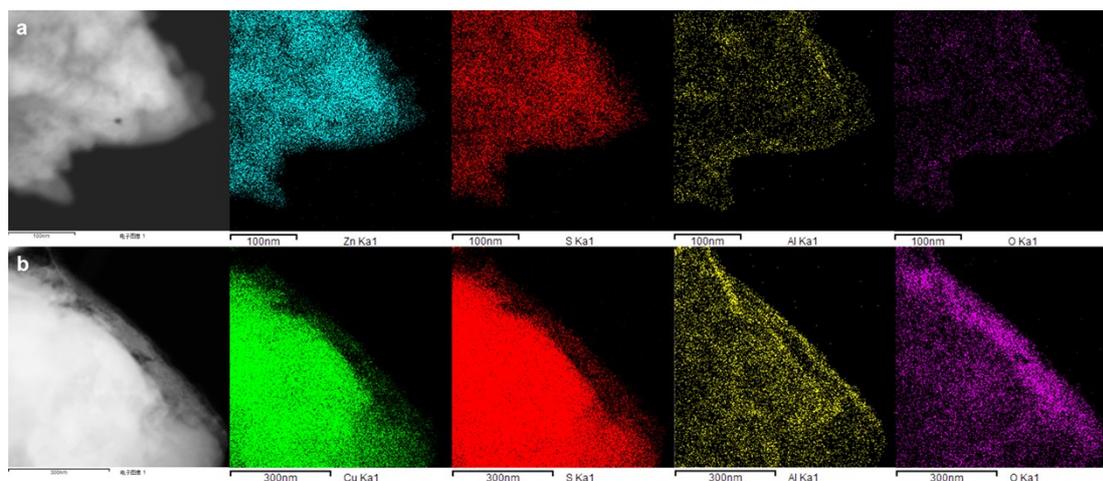
<sup>1</sup> The authors contributed equally in this work.



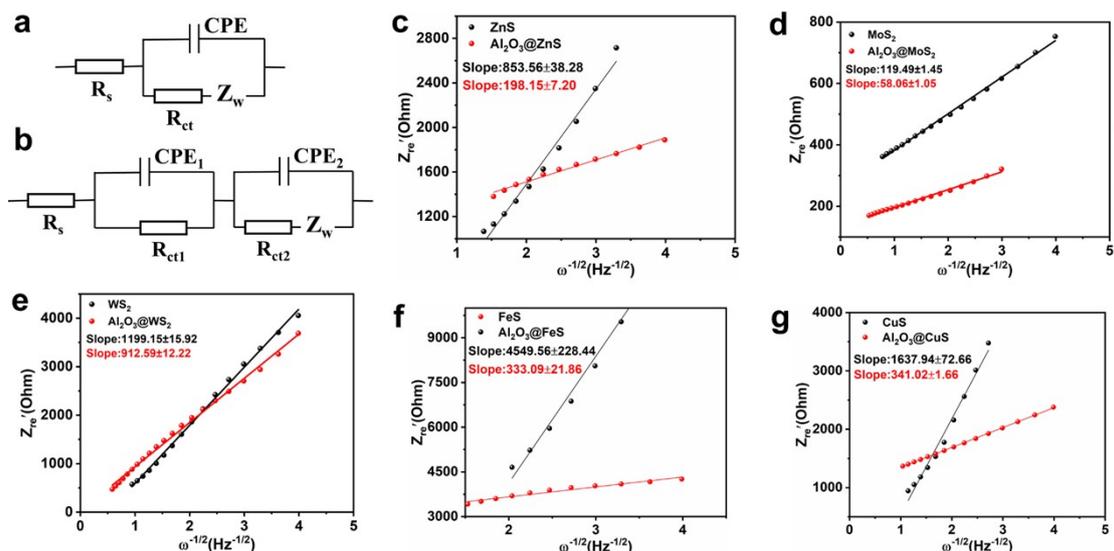
**Fig. S1** Nitrogen adsorption-desorption isotherms, BJH pore size distribution curves and specific surface area of freeze dried (a) pristine WS<sub>2</sub>, (b) pristine FeS samples.



**Fig. S2** Low magnitude TEM images of (a) ZnS, (b) MoS<sub>2</sub>, (c) WS<sub>2</sub>, (d) FeS, (e) CuS.



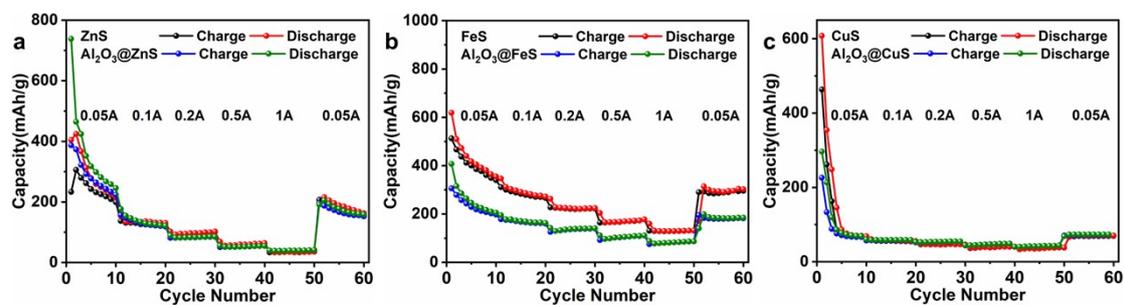
**Fig. S3** Elemental mappings of (a) Al<sub>2</sub>O<sub>3</sub>@ZnS and (b) Al<sub>2</sub>O<sub>3</sub>@CuS.



**Fig. S4** (a) Simulation circuit for bare TMSs, (b) simulation circuit for  $\text{Al}_2\text{O}_3@\text{TMSs}$ , the fitting lines in the low frequency region of (c) ZnS and  $\text{Al}_2\text{O}_3@\text{ZnS}$ , (d)  $\text{MoS}_2$  and  $\text{Al}_2\text{O}_3@\text{MoS}_2$ , (e)  $\text{WS}_2$  and  $\text{Al}_2\text{O}_3@\text{WS}_2$ , (f) FeS and  $\text{Al}_2\text{O}_3@\text{FeS}$ , (g) CuS and  $\text{Al}_2\text{O}_3@\text{CuS}$ .

**Table S1** EIS data of different samples before cycling ( $\sim\text{cm}^{-2}$ )

|                                      | $R_s$<br>( $\Omega$ ) | $\text{CPE}/\text{CPE}_1$<br>( $\text{S}\cdot\text{sec}^n$ ) | Frequent<br>power, n | $R_{ct}/R_{ct1}$<br>( $\Omega$ ) | $\text{CPE}_2$<br>( $\text{S}\cdot\text{sec}^n$ ) | Frequent<br>power, n | $R_{ct2}$<br>( $\Omega$ ) | Warburg<br>( $\text{S}\cdot\text{sec}^{-0.5}$ ) |
|--------------------------------------|-----------------------|--|----------------------|----------------------------------|---|----------------------|---------------------------|---|
| ZnS                                  | 7.22                  | $2.94 \times 10^{-6}$  | 0.83                 | 304.3                            | -   | -                    | -                         | $5.07 \times 10^{-4}$                           |
| $\text{Al}_2\text{O}_3@\text{ZnS}$   | 1.16                  | $6.02 \times 10^{-6}$  | 0.86                 | 399.2                            | $7.04 \times 10^{-4}$                             | 0.73                 | 1270                      | $5.82 \times 10^{-3}$                           |
| $\text{MoS}_2$                       | 3.39                  | $1.49 \times 10^{-5}$  | 0.81                 | 181.6                            | -   | -                    | -                         | $3.14 \times 10^{-3}$                           |
| $\text{Al}_2\text{O}_3@\text{MoS}_2$ | 1.81                  | $1.77 \times 10^{-5}$  | 0.83                 | 131.6                            | $8.98 \times 10^{-3}$                             | 0.69                 | 1332                      | $3.03 \times 10^{-3}$                           |
| $\text{WS}_2$                        | 12.27                 | $1.08 \times 10^{-5}$  | 0.83                 | 102.7                            | -   | -                    | -                         | $5.58 \times 10^{-4}$                           |
| $\text{Al}_2\text{O}_3@\text{WS}_2$  | 11.87                 | $1.47 \times 10^{-5}$  | 0.81                 | 186.0                            | $1.03 \times 10^{-3}$                             | 0.76                 | 6421                      | $2.24 \times 10^{-4}$                           |
| FeS                                  | 1.22                  | $5.69 \times 10^{-6}$  | 0.84                 | 413.1                            | -   | -                    | -                         | $7.06 \times 10^{-5}$                           |
| $\text{Al}_2\text{O}_3@\text{FeS}$   | 1.18                  | $3.91 \times 10^{-6}$  | 0.92                 | 185.6                            | $1.05 \times 10^{-5}$                             | 0.84                 | 1610                      | $6.85 \times 10^{-4}$                           |
| CuS                                  | 1.44                  | $7.52 \times 10^{-6}$  | 0.87                 | 188.3                            | -   | -                    | -                         | $1.12 \times 10^{-3}$                           |
| $\text{Al}_2\text{O}_3@\text{CuS}$   | 1.95                  | $9.71 \times 10^{-6}$  | 0.80                 | 527.9                            | $1.15 \times 10^{-4}$                             | 0.8                  | 708.6                     | $3.40 \times 10^{-3}$                           |



**Fig. S5** Rate performance of (a) ZnS and  $\text{Al}_2\text{O}_3@\text{ZnS}$ , (b) FeS and  $\text{Al}_2\text{O}_3@\text{FeS}$ , (c) CuS and  $\text{Al}_2\text{O}_3@\text{CuS}$ .

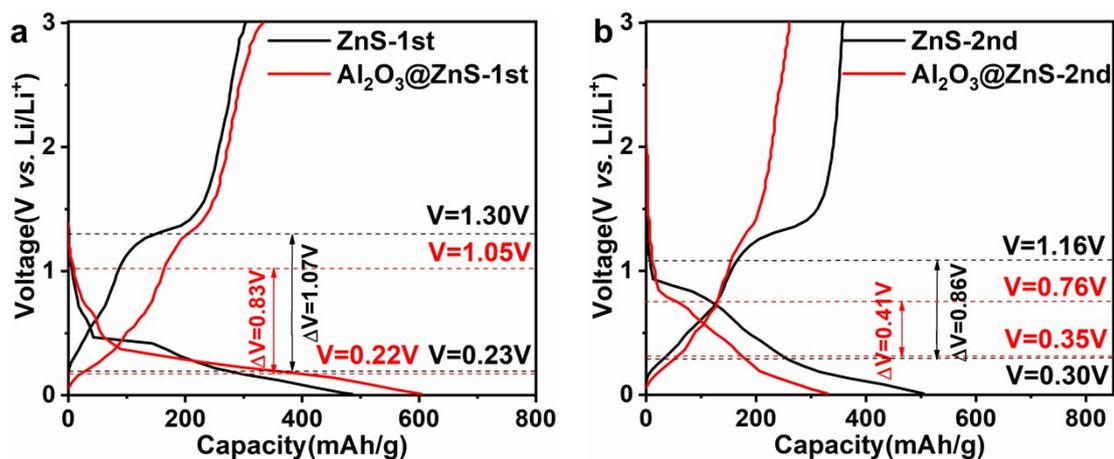


Fig. S6 Galvanostatic curves of ZnS and Al<sub>2</sub>O<sub>3</sub>@ZnS (a) 1<sup>st</sup> cycle, (b) 2<sup>nd</sup> cycle.

Table S2 The 1<sup>st</sup>-cycle coulombic efficiency of TMSs and Al<sub>2</sub>O<sub>3</sub>@TMSs anodes in Li half cells

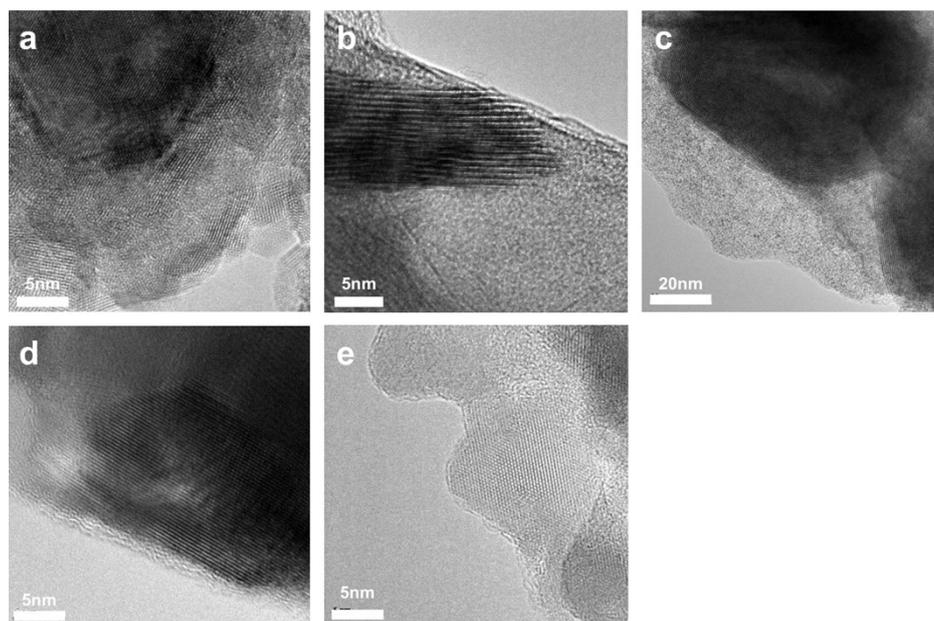
| sample   | Discharge capacity (mA·h·g <sup>-1</sup> ) | Charge capacity (mA·h·g <sup>-1</sup> ) | CE (%) |
|--|--|---|--------|
| ZnS  | 485.5                                      | 303.4                                   | 62.49  |
| Al <sub>2</sub> O <sub>3</sub> @ZnS              | 603.4                                      | 334.9                                   | 55.49  |
| MoS <sub>2</sub>                                 | 800.6                                      | 556.5                                   | 69.51  |
| Al <sub>2</sub> O <sub>3</sub> @MoS <sub>2</sub> | 588.6                                      | 426.4                                   | 72.44  |
| WS <sub>2</sub>                                  | 297.2                                      | 230.7                                   | 77.62  |
| Al <sub>2</sub> O <sub>3</sub> @WS <sub>2</sub>  | 606.5                                      | 443.3                                   | 73.09  |
| FeS  | 439.9                                      | 366.5                                   | 83.31  |
| Al <sub>2</sub> O <sub>3</sub> @FeS              | 490.4                                      | 355.2                                   | 72.44  |
| CuS  | 567.8                                      | 443.1                                   | 78.04  |
| Al <sub>2</sub> O <sub>3</sub> @CuS              | 523.0                                      | 414.6                                   | 79.26  |

Table S3 The 2<sup>nd</sup>-cycle coulombic efficiency of TMSs and Al<sub>2</sub>O<sub>3</sub>@TMSs anodes in Li half cells

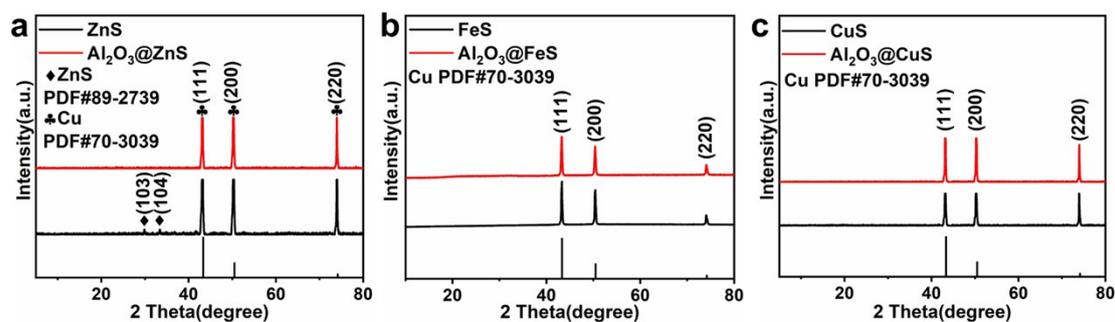
| sample   | Discharge capacity (mA·h·g <sup>-1</sup> ) | Charge capacity (mA·h·g <sup>-1</sup> ) | CE (%) |
|--|--|---|--------|
| ZnS  | 504.7                                      | 357.9                                   | 70.91  |
| Al <sub>2</sub> O <sub>3</sub> @ZnS              | 329.3                                      | 260.7                                   | 79.17  |
| MoS <sub>2</sub>                                 | 614.1                                      | 553.5                                   | 90.13  |
| Al <sub>2</sub> O <sub>3</sub> @MoS <sub>2</sub> | 580.1                                      | 526.5                                   | 90.76  |
| WS <sub>2</sub>                                  | 243.2                                      | 218.3                                   | 89.76  |
| Al <sub>2</sub> O <sub>3</sub> @WS <sub>2</sub>  | 385.1                                      | 440.8                                   | 87.36  |
| FeS  | 363.0                                      | 339.2                                   | 93.44  |
| Al <sub>2</sub> O <sub>3</sub> @FeS              | 346.0                                      | 300.9                                   | 86.96  |
| CuS  | 358.0                                      | 273.4                                   | 76.37  |
| Al <sub>2</sub> O <sub>3</sub> @CuS              | 328.0                                      | 254.0                                   | 77.44  |

**Table S4** The 5<sup>th</sup>-cycle coulombic efficiency of TMSs and Al<sub>2</sub>O<sub>3</sub>@TMSs anodes in Li half cells

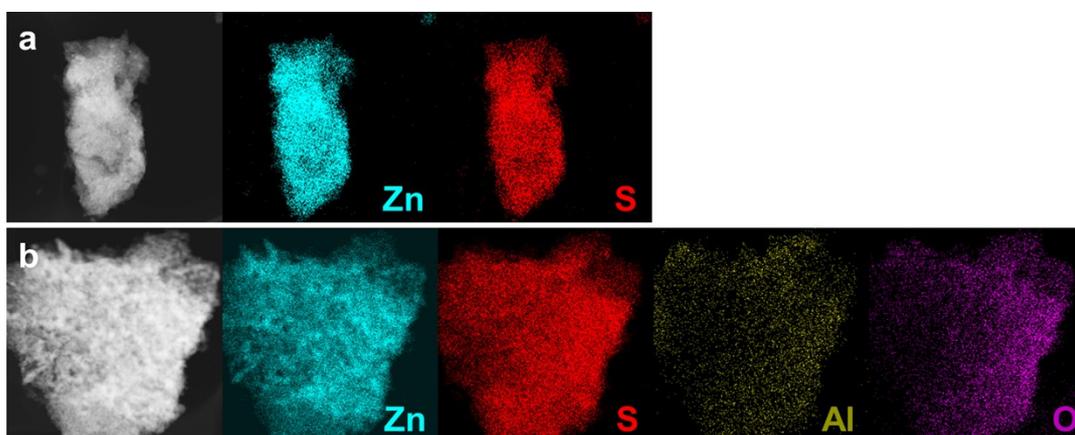
| sample   | Discharge capacity (mA·h·g <sup>-1</sup> ) | Charge capacity (mA·h·g <sup>-1</sup> ) | CE (%) |
|--|--|---|--------|
| ZnS  | 110.0                                      | 99.3                                    | 90.27  |
| Al <sub>2</sub> O <sub>3</sub> @ZnS              | 119.7                                      | 115.7                                   | 96.71  |
| MoS <sub>2</sub>                                 | 243.6                                      | 242.6                                   | 99.58  |
| Al <sub>2</sub> O <sub>3</sub> @MoS <sub>2</sub> | 316.7                                      | 310.9                                   | 98.16  |
| WS <sub>2</sub>                                  | 125.2                                      | 116.1                                   | 92.73  |
| Al <sub>2</sub> O <sub>3</sub> @WS <sub>2</sub>  | 139.4                                      | 132.3                                   | 94.91  |
| FeS  | 242.8                                      | 230.0                                   | 94.72  |
| Al <sub>2</sub> O <sub>3</sub> @FeS              | 194.9                                      | 186.0                                   | 95.44  |
| CuS  | 66.9                                       | 61.4                                    | 91.77  |
| Al <sub>2</sub> O <sub>3</sub> @CuS              | 77.5                                       | 68.4                                    | 88.19  |



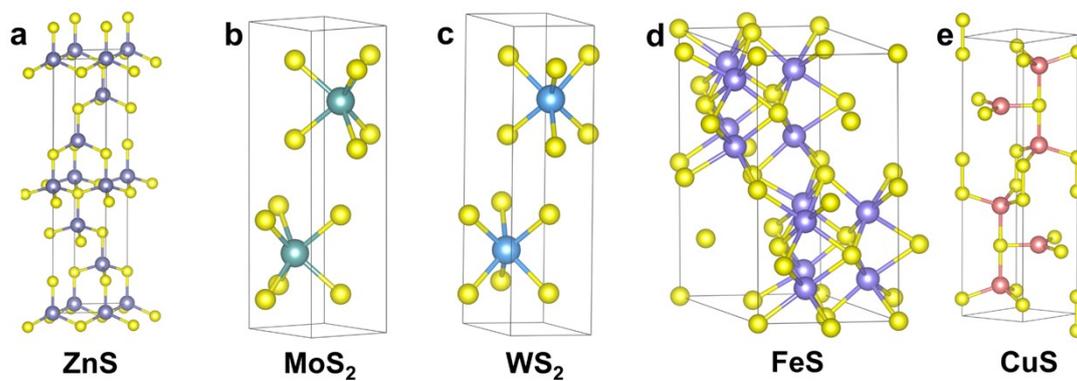
**Fig. S7** TEM images of TMSs that lithiated and delithiated for 1 cycle. (a) ZnS, (b) MoS<sub>2</sub>, (c) WS<sub>2</sub>, (d) FeS, (e) CuS.



**Fig. S8** XRD patterns of cycled samples. (a) ZnS and Al<sub>2</sub>O<sub>3</sub>@ZnS, (b) FeS and Al<sub>2</sub>O<sub>3</sub>@FeS, (c) CuS and Al<sub>2</sub>O<sub>3</sub>@CuS.



**Fig. S9** Elemental mappings of cycled (a) ZnS, (b) Al<sub>2</sub>O<sub>3</sub>@ZnS.



**Fig. S10** DFT calculation models. (a) ZnS, (b) MoS<sub>2</sub>, (c) WS<sub>2</sub>, (d) FeS, (e) CuS.