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Supporting Information

Field Emission from Vertically Oriented 2D Manganese Monosulfide Sheet

Derived from Chemical Route

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Figure S1

FIG.S1. (a) Powder X-ray diffraction (PXRD) pattern of Mn(OH)₂,(b)FESEM image of Mn(OH)₂.

Figure S2



FIG.S2. FESEM EDX elemental mapping of Mn₃O₄.



Figure S3

FIG.S3. FESEM EDX elemental mapping of MnS.





FIG.S4. Thermogravimetric analysis (TGA) of MnS.

Growth mechanism for the synthesis of Mn₃O₄ and MnS

Firstly, manganese chloride reacts with cetyltrimethylammonium bromide (CTAB) and has ability to coordinate with Mn⁺² ions in aqueous solution to form a stable complex ion [Mn(CTAB)]² and chloride ion (Cl-) released as counterions (pink solution) and sodium hydroxide (NaOH) reacts with cetyltrimethylammonium bromide (CTAB) to form precipitate. In the second step slowly add the solution of sodium hydroxide to the manganese chloride solution with continuous stirring. The addition of sodium hydroxide results in the formation of insoluble brown colour precipitates of manganese hydroxide (Reaction 1). The solution is washed with DI water and methanol to remove CTAB and other impurities.

$$MnCl_2(aq)+2NaOH(aq) \rightarrow Mn(OH)_2+2NaCl$$
 -----(1)

The third step involves the solid state reaction between the manganese hydroxide $Mn(OH)_2$ and sulfur powder (S) to form manganese sulfide (MnS). At elevated temperatures ,manganese hydroxide undergoes thermal decomposition to form manganese oxide intermediates. The manganese oxide intermediates then react with sulfur powder to form manganese sulfide and water vapour as a side product. The ion exchange reaction is an effective and low-cost method for chemical transformation of nanomaterials. The overall solid-state reaction is the combination of the decomposition of manganese hydroxide and the reaction with sulfur powder, leading to the formation of manganese sulfide (Reaction 2). The reaction occurs at elevated temperatures to provide sufficient energy for thermal decomposition of manganese hydroxide and the subsequent reaction with sulfur and in controlled atmosphere to prevent unwanted side reaction or oxidation of manganese species. The formation mechanism of Mn-S in our work is based on the anion exchange between OH- in the $Mn(OH)_2$ precursor with S²⁻ ions.

$$Mn(OH)_2(s) + S(s) \rightarrow MnS(s) + H_2O(g) + \frac{1}{2}O_2(g)$$
 -----(2)

For the synthesis of manganese oxide the thermal decomposition of manganese hydroxide involves the oxidation process converting Mn(II) to Mn(III) and Mn(IV) oxidation states (Reaction 3). The thermal decomposition of manganese hydroxide (Mn(OH)₂) occur when the compound is heated, leading to the release of water vapor and the formation of manganese oxide. The reaction involves breaking the bonds within the manganese hydroxide molecule, resulting in the release of water and the formation of manganese oxide. The manganese oxide product further reacts with oxygen in the air to form higher oxidation states.

$$3Mn(OH)_2(s) + \frac{1}{2}O_2(g) \rightarrow Mn_3O_4(s) + 3H_2O(g)$$
 ------(3)

The difference in morphology between Manganese(II) sulfide (MnS) and Manganese(II,III) oxide (Mn₃O₄) is attributed to the distinct crystal structures and chemical compositions of these two compounds. MnS typically crystallizes in different phases, including a zinc blende structure (cubic) or a wurtzite structure (hexagonal). In solvothermal methods, the reaction between manganese precursors and sulfur sources, under controlled conditions of temperature and pressure, can lead to the nucleation and subsequent growth of MnS crystals. The cause for drastic change in surface morphology of MnS is high energy anion exchange reaction kinetics between Mn(OH)₂ nanoparticles and S particles (Supplementary Figure S5) .During high reaction kinetics S²⁻ ions possess tremendously high kinetic energy constantly bombarding on Mn(OH)₂ nanoparticles and simultaneously exchange with (OH-) anions. Numerous pores

were created on the surface of MnS after the annealing treatment, due to the release of gaseous precursor during the annealing treatment which results in the formation of interconnected sheet like structure of manganese sulfide. Mn_3O_4 has a mixed valence structure, with a combination of Mn(II) and Mn(III) ions. The crystal structure is spinel, where oxygen atoms form a face-centered cubic lattice, and manganese ions occupy octahedral and tetrahedral sites within the lattice. The formation of Mn_3O_4 involves the oxidation of Mn(II) to Mn(III), and the growth is proceed through nucleation and subsequent crystal growth results in the formation of Mn_3O_4 nanoparticles.



FIG.S5. Growth mechanism for the synthesis Mn₃O₄ and MnS.