

Rapid solid-state synthesis of Mn_3O_4 nanocrystals at room temperature

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Experimental

Chemicals of hydrated manganese salt ($\text{MnSO}_4 \cdot \text{H}_2\text{O}$, $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ or $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (AR, Sinopharm Chemical Reagent Co., Ltd)) and NaOH (AR, Sinopharm Chemical Reagent Co., Ltd) in a mole ratio of 1:2.05 were mixed by ball-milling at 300 rpm for 30 min with changing the direction of rotation per 15 min. During the mixing process, the solid-state reaction between hydrated manganese salt and NaOH took place, and $\text{Mn}(\text{OH})_2$ was produced and air-oxidized. The obtained mixture was thoroughly washed by deionized water to remove sodium salts and residual NaOH, and then dried in vacuum at 80 °C.

For comparison, the reactions between manganese salts and NaOH in aqueous solution in a mole ratio of 1:2.05 were performed. For low-concentration reaction, the solution of 2.46 M NaOH was added dropwise to the solution of 0.3 M MnSO_4 and stirred in air at room temperature for 30 min, and then the suspension was filtered and fully washed by deionized water, and finally dried in vacuum at 80 °C. The high-concentration reaction between 3 M MnSO_4 solution and 24.6 M NaOH solution was

also performed.

The crystalline phase of the reaction products were identified by X-ray diffraction (XRD, Rigaku-TTRIII18kW) utilizing CuK_α radiation. The particle morphology and size of the products were observed by scanning electron microscopy (FE-SEM, ThermoScientific Apreo 2C) and transmission electron microscopy (TEM, FEI Tecnai G2 TF30). Magnetic properties were measured on a physical properties measurement system (PPMS DynaCool-14T, Quantum Design).

Supplementary figure

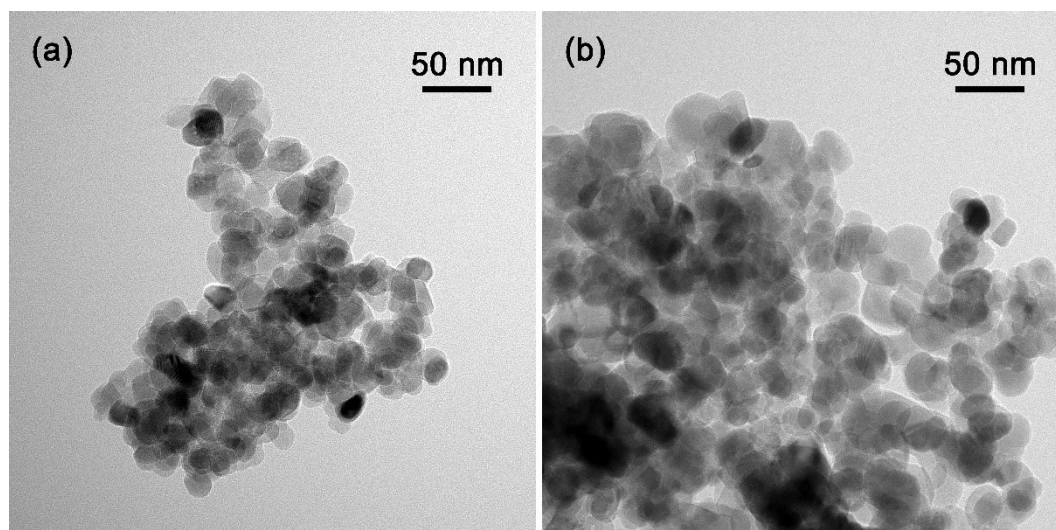


Fig. S1 TEM images of the washed products from the solid-state reactions of (a) $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ and (b) $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ with NaOH.

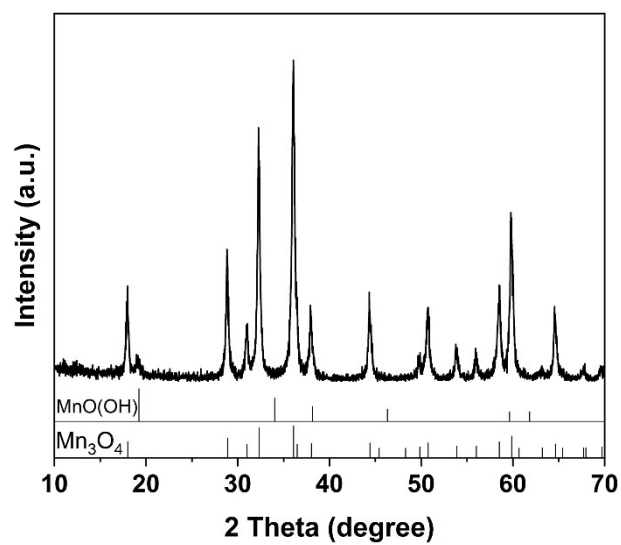


Fig. S2 XRD pattern of the washed product by the solid-state reaction of $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ with 20% excess NaOH.