

Methods

Materials. First of all, porous micron-sized composite calcium-based materials (CM) is prepared by sol-gel method. Calcium nitrate (Aladdin 99%), aluminum nitrate (Aladdin 99%), Iron (III) ferric nitrate (Aladdin 99%) is added to citric acid after doping according to the mole ratio of 100:10: 5. Where the molar ratio of cationic to citric acid is 1: 1.5. Then add appropriate amount of deionized water and heat it in a water bath at 90 °C for 4 hours until the solution becomes gel. Then calcinate it in a muffle furnace at 800 °C for 4 hours to obtain the CM.

Secondly, NTEP of NdMnO_3 is prepared by sol-gel method. Manganese nitrate solution (Aladdin 50%wt) and neodymium nitrate solution (Aladdin 99%) are mixed in a molar ratio of 1:1, and then citric acid is added, wherein the molar ratio of cations to citric acid is 1:1.5. After mixing under a magnetic stirrer, measure the pH value with a pH meter. If the pH is less than 6, add ammonia water to control it between 6-7 to ensure the synthesis of single-phase neodymium manganate crystals. Then, the sol is formed after stirring and heating in a water bath at 90° C for 6 hours. Finally, dry at 120°C for 12 hours and calcinate in a muffle furnace at 1000°C for 5 hours to obtain the NTEP.

Composite millimeter-scale calcium-based particles are prepared by solid-state synthesis and mechanical extrusion. Calcium hydroxide (Aladdin 99%), aluminum nitrate (Aladdin 99%), Iron (III) ferric nitrate (Aladdin 99%), and NTEP are mixed according to the molar ratio of 10:1:1:0.5, and then add microcrystalline cellulose (Aladdin MCC) to ensure that the mass ratio of MCC to calcium hydroxide is 1:5, fully

grind for 1 hour to obtain composite calcium oxide powder. Then the particles with a diameter of 1 mm are obtained by mechanical extrusion¹. Finally, it is calcined at 900°C for 3 hours to obtain composite millimeter-scale calcium oxide particles.

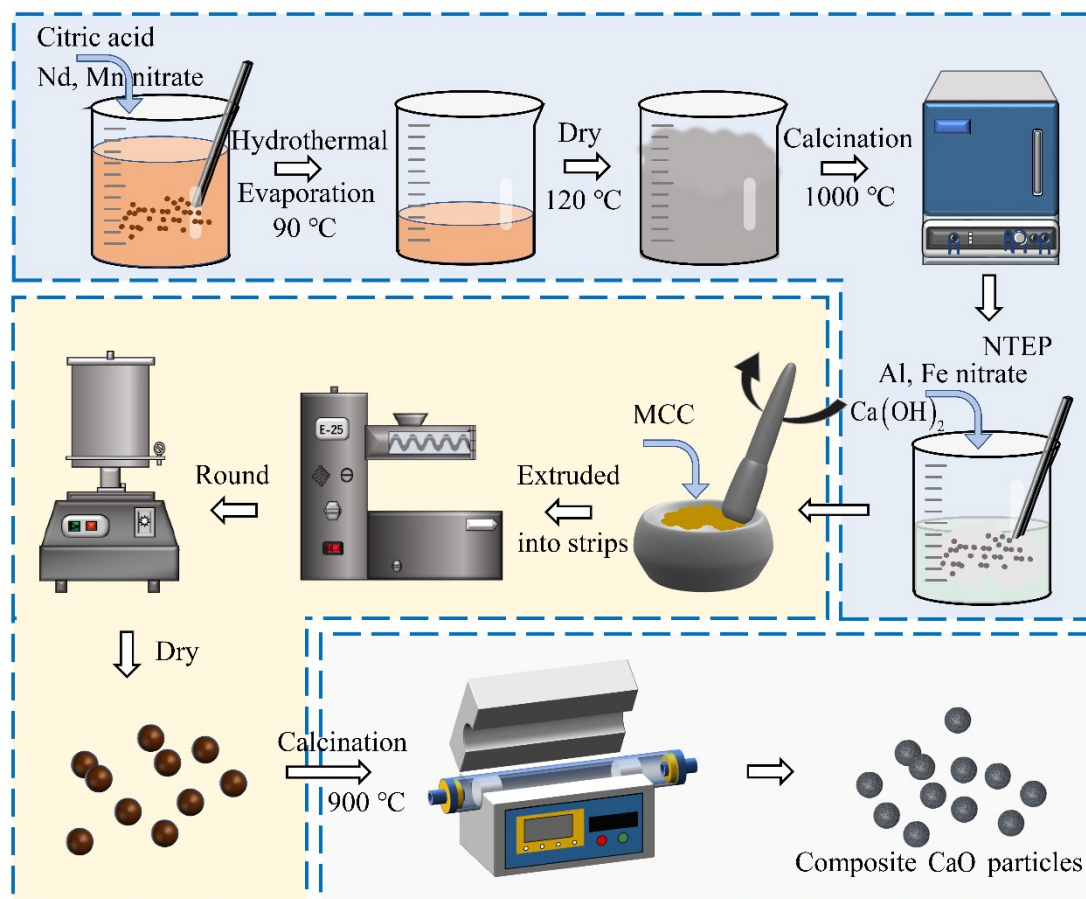


Fig. S1. Preparation steps of composite calcium oxide particles.

Measurements. The phase composition of NTEP, composite calcium oxide and pure calcium oxide is determined by X-ray diffraction (D8 ADVANCE, Bruker, Germany) analysis method. In order to compare the negative thermal expansion properties after adding NTEP, the linear thermal expansion coefficient from 500 °C to 800 °C (heating rate 5 °C/min) is measured using a thermal dilatometer (DIL402c, Netzsch). At the same time, the cycle stability and energy storage density of the composite calcium oxide particles are tested with a thermogravimetric analyzer (SDT650, TA Instruments,

USA). The operating program is to rise from normal temperature to 750 °C at a rate of 20 °C/min, then drop to 600 °C after 30 minutes of heat preservation, and then gradually increase the temperature to 700 °C at 10 °C/min, during which it is acidified in CO₂ gas. After the acidification, the gas is switched to N₂ for calcination at 700 °C for 20 minutes, and finally the temperature is changed between 600 °C and 700 °C for 260 times. The mass of the sample taken for each test is about 1-3 mg. Besides, the spectral absorptivity is obtained with a UV-Vis-NIR spectrophotometer (LAMBDA 1050+ PerkinElmer, USA) ². Finally, the microscopic morphology under different cycle times is analyzed by a field emission scanning electron microscope (FESEM-Gemini SEM 300 Zeiss, Germany).

Computational methods. The structure of NdMnO₃ is optimized and the electronic properties are calculated using the VASP software package (version 5.4.1) based on density functional theory (DFT). A high-precision lattice optimization has been carried out on the NdMnO₃ unit cell composed of 18 atoms. We use the Perdew-Burke-Ernzerhof (PBE) exchange correlation (XC) functional of the generalized gradient approximation (GGA) for the calculations. ³⁻⁵ The plane wave cutoff energy is 400 eV. The Brillouin band is sampled using the Monkhorst-Pack scheme. The structure is fully relaxed with a gamma center of 3×2×3 k-mesh. In the calculation of phonon correlation, the PHONOPY software package ⁶ is used. In order to eliminate possible imaginary frequencies, all models are expanded into 2×2×2 supercells, all atoms are fully relaxed, and the convergence accuracy of the force is 10⁻⁷ eV/Å, and the energy convergence accuracy is 10⁻⁸ eV. After the optimized crystal structure, 11 crystal models are

constructed by modifying the scaling factor to 0.95-1.05, and the phonon spectrum is calculated by the finite displacement method, and the thermal expansion coefficient of the material is calculated by QHA (Quasi harmonic approximation). Substituting the phonon density of state function $g(\omega)$ and frequency $\omega = \omega(V)$ into the phonon free energy $F_{ph}(T, V)$ can be obtained:

$$F_{ph} = \int_0^{\infty} g(\omega) d\omega \left[\frac{\hbar\omega}{2} + k_B T \ln(1 - \exp(-\frac{\hbar\omega}{k_B T})) \right] \quad (1.1)$$

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where the Helmholtz free energy of the system can be written as:

$$F(T, V) = F_{ph}(T, V) + E(V) \quad (1.2)$$

With the help of the Vinet equation of state (Equation of state, EOS) ⁷, the adiabatic F-V curve is fitted, and the lowest energy point is found on a series of F-V curves, and then fitted to obtain the thermodynamic function related to temperature, including the thermal expansion coefficient. It can be seen from Fig.S2(d) that the linear thermal expansion coefficient of NdMnO₃ decreases from 600 to 800 °C, which also verifies the authenticity of the experiment.

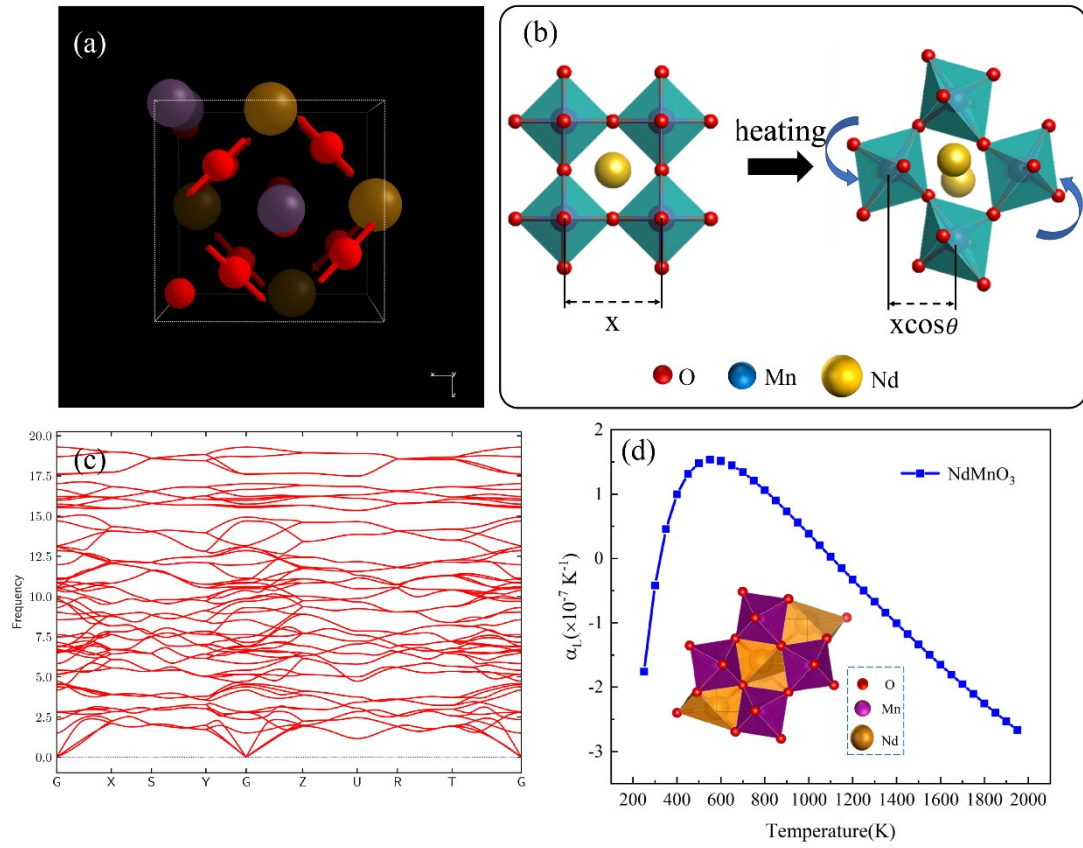


Fig. S2. Computational models and results: (a) is the schematic diagram of atomic vibration and (b) is the schematic diagram of crystal structure, (c) is the phonon Spectrum and (d) is the calculated thermal expansion coefficient curve.

Table S1. Comparison of energy storage density and other parameters in references and this work.

Sample No.	Solar absorption (%)	Cycle number	Energy storage density (kJ/kg)	Refs
ZrO ₂ (40 wt%)	/	50	813	8
Ca/Mg ₂ Mn ₄ Fe	63.7	15	1666	9
D-CaCO ₃	80.3	15	1875	10
15-6-12-1.5-0.5	78.98	15	1888	11
100-5-10-5	90.8	15	2352	This work

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