Rapid room-temperature synthesis of nanocrystalline spinels as oxygen reduction and evolution electrocatalysts

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Spinels can serve as alternative low-cost bifunctional electrocatalysts for oxygen reduction/evolution reactions (ORR/OER), which are the key barriers in various electrochemical devices such as metal-air batteries, fuel cells and electrolyzers. However, conventional ceramic synthesis of crystalline spinels requires an elevated temperature, complicated procedures and prolonged heating time, and the resulting product exhibits limited electrocatalytic performance. It has been challenging to develop energy-saving, facile and rapid synthetic methodologies for highly active spinels. In this Article, we report the synthesis of nanocrystalline M$_x$Mn$_{3-x}$O$_4$ (M = divalent metals) spinels under ambient conditions and their electrocatalytic application. We show rapid and selective formation of tetragonal or cubic M$_x$Mn$_{3-x}$O$_4$ from the reduction of amorphous MnO$_2$ in aqueous M$^{2+}$ solution. The prepared Co$_x$Mn$_{3-x}$O$_4$ nanoparticles manifest considerable catalytic activity towards the ORR/OER as a result of their high surface areas and abundant defects. The newly discovered phase-dependent electrocatalytic ORR/OER characteristics of Co-Mn-O spinels are also interpreted by experiment and first-principle theoretical studies.

As a result of their diverse properties, spinel compounds of AB$_2$X$_4$ (A,B = metal, X = chalcogen) have attracted a great deal of research interest linked to a wide range of applications including magnetism, electronics and catalysis, as well as energy storage and conversion1–3. The spinel structure is known to be built around a closely packed array of X$^{2–}$ ions, with A$^{2+}$ and B$^{3+}$ cations occupying part or all of the tetrahedral and octahedral sites, respectively4. Among the numerous varieties of spinels, MMn$_3$O$_4$ is one of the most intriguing composite oxides, because manganese has many advantages, including low cost, high abundance, low toxicity, multiple valence and prominent Jahn–Teller effect5. Manganese-based spinels have a range of versatile applications, including lithium insertion electrodes6, magnetic materials7 and catalysts8. Their physicochemical properties are highly sensitive to the composition, structural parameters, and distribution and oxidation state of cations5–8, which depend greatly on the synthesis conditions. The traditional synthesis of spinel compounds generally follows a solid-state route that involves grinding and firing of a mixture of oxides, nitrates or carbonates9. Solid-state reactions generally require elevated temperatures or prolonged process times to overcome the diffusional barriers10,11. Recently, to replace such conventional 'brute force' ceramic preparations, developments have been made in new approaches such as sol–gel processing12, organic co-precipitation13 and flux or solvothermal strategies14. These can proceed at moderate temperatures and form metastable phases with controllable product particle size due to enhanced reaction kinetics. However, despite continuous efforts, the rapid and rational synthesis of crystalline spinels at room temperature and ambient atmosphere remains a challenge.

The oxygen reduction/evolution reactions (ORR/OER) play key roles in many energy conversion and storage technologies, including metal–air batteries, fuel cells and electrolyzers15. ORRs are sluggish in nature and traditionally require the exclusive use of platinum-based catalysts15,16. As platinum is expensive and scarce, substantial efforts have been dedicated to further improving its performance, and also to searching for non-noble metal catalysts17–20. Spinels can be used as alternative and low-cost electrocatalysts for ORRs and OERs21,22. However, spinels prepared by the traditional ceramic route have limited electrocatalytic activity due to their large particle size and low specific surface areas. The development of nanostructured spinels suitable for the highly efficient catalysis of ORRs/OERs is therefore of paramount importance.

In this Article, we present a facile and rapid methodology to prepare the nanocrystalline spinel M$_x$Mn$_{3-x}$O$_4$ (M represents divalent metals such as Co, Mg and Zn) under ambient conditions, as well as the application of the synthesized nanoparticulate Co$_x$Mn$_{3-x}$O$_4$ as a bifunctional electrocatalyst for both ORR and OER. The formation of M$_x$Mn$_{3-x}$O$_4$ was accomplished by reduction of amorphous MnO$_2$ precursors in an aqueous solution containing M$^{2+}$. Amorphous MnO$_2$ nanoparticles were selected as precursors because they result in short diffusion distances and high surface areas for facile solid-state diffusion and interfacial contact, and also offer linked building blocks ([MnO$_4$]$^{4–}$ octahedrons), which are partially retained as a moiety in the final product. The randomly arranged structural units in amorphous MnO$_2$ also aid lattice reconstruction during its transformation into crystalline spinels, because of its lower activation energy barrier. We also combine evidence from both experiment and density functional theory (DFT) to determine the high catalytic activity of the Co–Mn–O nanocrystalline spinels and the related phase-dependent electrochemical characteristics that have not been investigated previously. It was found that the cubic Co–Mn–O spinel outperforms the tetragonal phase in intrinsic ORR catalytic activity, but the tetragonal spinel surpasses the cubic phase for OER, due to the dissimilar binding energies of oxygen adsorption on cobalt and manganese defect sites.
Results and discussion

We have achieved the room-temperature synthesis of manganese-based spinels by chemical reduction of MnO₂ in the presence of metal ions. The amorphous MnO₂ precursor with a mean manganese valence of 3.7 was first prepared in a one-step redox reaction between KMnO₄ and Mn(CH₃COO)₂ in alkaline aqueous solution (Supplementary Figs S1 and S2). Two representative nanocrystalline Co₃MnO–B and CoMnO–P, were then synthesized using NaH₂PO₂ and NaBH₄ as reductants, respectively.

Figure 1 shows the X-ray diffraction (XRD) patterns and corresponding Rietveld analysis of as-prepared samples, confirming the XRD analysis. TEM imaging of CoMnO–B (Fig. 2a) and CoMnO–P (Fig. 2b) confirm the elemental composition determined by energy-dispersive spectra (EDS) of CoMnO–P and CoMnO–B (Fig. 2f) confirm the elemental composition determined from atomic absorption spectroscopy.

Three points are worth highlighting regarding the present synthesis of nanocrystalline spinels. First, the synthesized phase was determined by the reducing ability of the applied reductant. Strong reducing agents such as NaBH₄ and N₂H₄·H₂O (Supplementary Fig. S5) resulted in tetragonal spinels with the composition of CoMnO₄. In contrast, when NaH₂PO₂, with its relatively weak reducing power, was used, Mn(Ⅲ) in the MnO₂ precursor was only partially reduced to form a cubic phase, and the remaining high-valence manganese resulted in a birnessite phase. This phase selectivity could be explained by taking into account the fact that Mn(Ⅲ) (d⁵) tends to Jahn–Teller distortion⁵, and thus induces lower crystallographic symmetry. The second point is that phase speciation of spinels was accomplished within a short time period (Supplementary Fig. S4) is basically preserved. The average particle size of CoMnO–P increased from ~70 nm to 110 nm, whereas CoMnO–B demonstrated a rectangular and porous texture. The interconnected porous structure of CoMnO–B could be attributed to hydrogen bubbling from the reaction between MnO₂ and BH₄⁻. The clear fringes observed in transmission electron microscopy (TEM) images and the corresponding fast Fourier transform (FFT) diffraction pattern (Fig. 2c,d) indicate the crystallinity of the synthesized nanoparticles, in spite of the presence of numerous defects. The measured neighbouring interlayer distance in CoMnO–P was consistent with the spacing between the (011) planes of the single tetragonal CoMnO₄ spinel phase, confirming the XRD analysis. TEM imaging of CoMnO–P also determined the coexisting phases of cubic spinel and monoclinic birnessite, with indexed planes of (111) and (202), respectively.

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The well-defined points in the FFT pattern agree with the allowed Bragg diffraction of cubic spinel. Furthermore, results from the energy-dispersive spectra (EDS) of CoMnO–P (Fig. 2e) and CoMnO–B (Fig. 2f) confirm the elemental composition determined from atomic absorption spectroscopy.
time (5 min; Supplementary Fig. S6), enabling a rapid synthesis that is barely achievable using traditional high-temperature ceramic routes. Third, the non-crystallinity of the MnO₂ precursor is a critical influential factor in obtaining a spinel product under ambient conditions. High-purity spinels could be prepared only from amorphous MnO₂ rather than from crystalline MnO₂ (Supplementary Fig. S2), because in the latter case the formation of spinel requires more energy to overcome the higher energy barrier accompanying the collapse of the ordered parent crystal lattice. Increasing the concentration of reducing agent or elevating the reaction temperature could enhance the crystallinity of the formed spinels (Supplementary Table S5). Furthermore, it is possible to adjust spinel morphology by altering the shape of the precursor. In addition to nanoparticles, interconnected wirelike Co–Mn–O nanostructures were also fabricated using electro-deposited amorphous MnO₂ nanowires (Supplementary Fig. S7).

The question emerging from this experiment is why nanocrystalline spinels can be formed at room temperature and under ambient pressure. We found that, in the absence of Co³⁺, the reduction of amorphous MnO₂ resulted in high-purity Mn₃O₄ with a typical tetragonal spinel phase (Supplementary Fig. S8). The standard Gibbs free energy change of the pertinent reaction (3 MnO₂ + BH₄⁻ → Mn₃O₄ + BO₂⁻ + 2 H₂) is ~681 kJ mol⁻¹, indicating that the formation of spinel from MnO₂ is thermodynamically feasible (see Supplementary Information). Accordingly, we propose a reduction–crystallization mechanism for the synthesis of CoₓMn₃₋ₓO₄. The Mn(IV) in the amorphous nanoparticulate MnO₂ precursor is rapidly reduced to lower-valence manganese (Mn(III) and/or Mn(II)) by a strong reducing agent²³, and the amorphous MnO₂ structure is transformed to the spinel phase. At the same time, the dissociative Co²⁺ in the solution diffuses into the solid lattice and either occupies the manganese vacancies or partially substitutes for manganese ions in the tetrahedral or octahedral inter-space. The driving force of such ion exchange is the 'site preference energies' of transition-metal ions in the spinel crystal lattices, according to crystal field theory.²⁵,²⁶ The Co–Mn–O solid solution spontaneously crystallizes into the final nanocrystalline spinel and maintains the essential morphology of the precursor. Based on this postulated synthetic route, we have also successfully prepared ZnMn₂O₄ and MgMn₂O₄ crystalline nanoparticles.

Figure 2 | Characterization of CoMnO-B and CoMnO-P. a, b, SEM images showing the porous nanostructures of CoMnO-B (a) and the nanoparticulate morphology of CoMnO-P (b). c, d, High-resolution TEM images and the corresponding FFT patterns (inset), showing the single tetragonal spinel phase (c) and the double phases of cubic spinel and monoclinic birnessite (d). e, f, EDS spectra confirming the elemental ratio of cobalt to manganese.
through similar procedures by simply replacing Co$^{2+}$ with Zn$^{2+}$ and Mg$^{2+}$, respectively (Supplementary Fig. S9).

Because of the nanoparticulate texture, the prepared representative CoMnO–B and CoMnO–P spinels had Brunauer–Emmett–Teller (BET) surface areas of 112 and 122 m$^2$ g$^{-1}$, respectively, which are significantly higher than those of the tetragonal CoMn$_2$O$_4$ (denoted HT-T-spinel) and cubic Co$_2$MnO$_4$ (denoted HT-C-spinel) powders synthesized using the traditional high-temperature method (Supplementary Figs S10 and S11). The featured high specific areas and numerous defects of nanocrystalline spinels motivated us to further investigate their catalytic performance for ORR/OER.

Figure 3 shows the ORR and OER catalytic characteristics recorded on glass carbon electrodes loaded with the CoMnO–B and CoMnO–P nanoparticles and the corresponding high-purity spinel powders synthesized at high temperature. As shown in Fig. 3a, the representative linear sweeping voltammograms of the ORR, measured on rotating disk electrodes (RDEs), exhibited similar profiles, with two regions of potential–current response. Scanning the potential cathodically, the detected currents increased rapidly in the mixed kinetic–diffusion control region (approximately −0.1 to −0.3 V) and then slowed down, with the appearance of diffusion-limiting currents ($I_D$). As has been reported for other transition-metal oxides$^{27,28}$, the observed current was attributed to catalytic oxygen reduction through comparison with polarization curves recorded on the electrodes without catalyst modification or in the absence of oxygen, which showed no distinguishable cathodic current over the tested potential range (Supplementary Figs S12 and S13). Evidently, the room-temperature nanocrystalline spinels outperformed the corresponding high-temperature spinel powders in terms of more positive onset potential and larger current value. Furthermore, the cubic phase exhibited lower overpotential than did the tetragonal phase (Supplementary Figs S14 and S15).

To quantitatively analyse the catalytic ORR, four sets of voltammetry curves were recorded on RDEs at different speeds of rotation (Supplementary Fig. S13). The current increased with rising rotational rates as a result of the faster oxygen flux to the electrode surface. The observed rotation-speed-dependent current $I$ can be theoretically expressed by the Koutecky–Levich (K–L) equation$^{29}$ for analysing ORR kinetics (see Supplementary Information). Figure 3b shows the constructed K–L curves, which plot $1/I$ versus $\omega^{-1/2}$ at −0.5 V, where the transferred electron number per oxygen molecule ($n$) in the ORR can be calculated from the slopes of the fitted linear line. Lower $n$ values indicate inferior performance. These results suggest an apparent quasi-four-electron process on nanocrystalline spinels, which is desirable for achieving high-efficiency electrocatalytic ORR. Among the spinels, catalytic activity decreased in the order CoMnO–P > CoMnO–B > HT-C-spinel > HT-T-spinel. As the two high-temperature samples were of high purity, comparison of their performance directly reflects the different intrinsic activities of the cubic and tetragonal phases. For spinels with the same phase, room-temperature nanoparticles outperform their high-temperature counterparts. Such superior activity could be largely attributed to the higher specific surface areas of nanocrystalline spinels providing more active sites for heterogeneous ORR catalysis.

For the nanocrystalline spinels, the steady currents observed in the continuous polarization period of 2 h (Supplementary Fig. S16) provided preliminary evidence of catalytic stability in an alkaline medium, which is consistent with previous results for manganese-based oxides$^{30}$. The ORR performance of the four spinel samples was compared with the benchmark carbon-supported platinum nanoparticles (Pt/C) (Supplementary Fig. S17 and Table S6). Surprisingly,
The nanoparticulate spinels exhibited currents and apparent transferred electron numbers close to those of the Pt/C catalyst. The relatively lower onset potential for the spinels could be improved by cation doping or metal decorating to modify the surface electronic properties or enhance conductivity. The nanocrystalline spinels also demonstrated favourable ORR activity in neutral KCl electrolytes (Supplementary Fig. S18). Furthermore, the most active catalyst was used in an air electrode to construct a laboratory coin-type zinc–air battery. Therefore, it is clear that nanocrystalline spinels synthesized at room temperature should find a practical application in metal–air batteries.

Spinel metal oxides have been widely investigated as a catalyst for OER, so we next measured the quasi-steady polarization curves in a solution of 0.1 M KOH in the potential range 0.6–1.0 V (Fig. 3d). We conducted a series of DFT calculations (see computational details in the Supplementary Information) to study the oxygen adsorption on different defect sites of two typical surfaces, cubic (113) and tetragonal (121). Figure 4a–d displays the binding energies ($E_b$) of an oxygen molecule on Co/Mn defect sites of the as-investigated spinel phases. It is clear that the cobalt defect site can bind oxygen a little more strongly than the manganese defect site, whereas, on either the cobalt or manganese sites, the cubic (113) phase generates much more stable molecular oxygen adducts than the tetragonal (121) surface. Figure 4e,f presents oxygen adsorption characteristics from the electron structure analysis aspect. In comparison with the tetragonal spinel, the cubic phase shows an increase in the adsorbed oxygen ($O_{ads}$)-induced $d$-band, indicating a strengthened metal–$O_2$ bond. Furthermore, the investigated surfaces of both phases contain the same number of catalytic sites per surface unit cell, but the area of the cubic (113) unit cell is smaller. Therefore, for a given surface area, the number of available active sites on the cubic (113) surface will exceed that on the tetragonal (121) surface. Accordingly, this can be interpreted to indicate that the cubic Co–Mn–O spinel outperforms the tetragonal phase in intrinsic ORR catalytic activity. Similarly, regarding electrocatalytic OER, one can predict that the performance of the tetragonal spinel surpasses the cubic phase, because the OER can be viewed as a reverse process of the ORR.

**Figure 4 |** First-principle study of surface oxygen adsorption on different sites of cubic and tetragonal spinel phases. a–d. Geometries and binding energies of oxygen molecules (purple) on cobalt (cyan) or manganese (grey) defect sites. Red spheres represent lattice oxygen. e,f. Corresponding density of states of bare and $O_2$-adsorbed spinels.

Conclusions

Rapid synthesis of nanocrystalline $M_xMn_{3−x}O_4$ ($M = Co, Mg, Zn,$ and so on) spinels at room temperature was realized using a reduction-recrystallization route with amorphous MnO$_2$ nanoparticles as precursors. The obtained $Co_{x}Mn_{3−x}O_4$ spinel, with controllable crystallographic phase of either the cubic or tetragonal form, inherits the essential morphology of the parent MnO$_2$, demonstrating high specific surface areas and abundant defects. When applied as an electrocatalyst for both ORR and OER, the room-temperature nanoparticles outperform the corresponding high-temperature powders. The intrinsic electrocatalytic activity of cubic and
tetragonal Co–Mn–O spinels correlates with the oxygen binding ability on the catalyst surface, as indicated from both experimental analysis and DFT theoretical calculations. These results should aid in the rational design and facile preparation of a spinel-based ORR/OER bifunctional electrocatalyst to be used in the air electrodes that are widely used in metal–air batteries and fuel cells.

Methods

Synthesis. To obtain amorphous MnO2 nanoparticle precursors, Mn(CH3COO)2 (100 ml, 0.03 M) was added to K2MnO4 solution (50 ml, 0.04 M, adjusted pH value of 12) at room temperature. The formed brown deposit was filtered, washed with water, and dried overnight at 60 °C. In a typical synthesis of nanocrystalline CoMn1– x O2 spinel, amorphous MnO2 (0.348 g) and CoCl2·6H2O (0.476 g) were mixed in 20 ml of water. Under vigorous magnetic stirring, an excess amount of freshly prepared NaBH4 solution (NaBH4 dissolved in NaOH solution, pH = 11–12) was then added dropwise to the mixture at controlled temperature. The violet-red solution immediately turned colourless, with severe bubbling. The resulting precipitate was collected by centrifugation, washed repeatedly with distilled water to remove residual ions, and vacuum-dried at 80 °C for 12 h. Similar procedures were adopted when using NaH2PO2 or N2H4·H2O as the reductant. For the synthesis of ORR bifunctional electrocatalyst to be used in the air electrodes that are widely used in metal–air batteries and fuel cells.

Characterization. XRD patterns were recorded on a Rigaku D/MAX-2500 X-ray diffractometer (Cu Kα radiation, λ = 1.5406 Å, in a 2θ range of angular range of 10–80° with a velocity of 0.02° in 4 s). The XRD profiles were refined using the Rietveld refinement program RIETAN-2000 (ref. 34). Chemical composition was determined by atomic absorption spectrometry (AAS, Hitachi 180-80 spectrophotometer) and EDX. SEM images were obtained using a JEOL JSM-6700F microscope (operating voltage, 10 kV) equipped with an EDS spectrometer. TEM and HRTEM images were collected on a Tecnai F20 (200 keV) microscope. Textural characterization was carried out by measuring the N2 adsorption/desorption isotherms at 77 K on a Bel kissne instrument. XPS data were collected using a Perkin Elmer PHI 1600 ESCA system. TPD/MS analysis was performed on an Autosorb-1C-TCDS MS system with a Prismaplus QME 220 MS detector (Quantachrome) under helium gas flow.

Electrochemical test. Electrochemical measurements were conducted using three-electrode cells. A glassy carbon disk electrode with coated catalysts was used as the working electrode. The catalyst was well-mixed with 30 wt% CoMn1– x O2 samples and 70 wt% carbon powders (Vulcan XC 72). The preparation of catalyst–carbon pastes was carried out by mixing 30 wt% CoMn1– x O2 with 70 wt% carbon powders (Vulcan XC 72). The preparation of catalyst–carbon pastes was carried out by mixing 30 wt% CoMn1– x O2 with 70 wt% carbon powders (Vulcan XC 72).

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Author contributions

E.C. performed the experimental work and characterized the materials. F.C. and J.S. carried out electrochemical measurements. B.P. performed the first-principles simulation. All authors contributed to the data analysis. J.C. directed the research.

Additional information

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