Supplemental Information

Template-free Synthesis of Mesoporous and Crystalline Transition Metal Oxide Nanoplates with Abundant Surface Defects

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1. Chemicals and Materials
All chemicals used were of analytical grade and used as received without further purification. Cobalt(II) nitrate hexahydrate, manganese(II) nitrate tetrahydrate, copper(II) nitrate trihydrate, zinc(II) nitrate hexahydrate, urea and 3,3',5,5'-tetramethylenediamine (TMB) were purchased from Sigma-Aldrich. Oleic acid was purchased from Alfa Aesar. Deionized water (High-Q, Inc. 103S Still) with a resistivity of >10.0 MΩ was used in all experiments.

2. Preparation of mesoporous Co₃O₄ and CoO nanoplates
In a typical synthesis of mesoporous Co₃O₄ nanoplates, 0.5154 g of urea was firstly dissolved in 10 mL of deionized water to obtain a homogeneous solution. After this, 15 mL of ethanol was added to the solution, stirred for 30 minutes. Four mL of oleic acid was then added to the above solution, stirred for another 30 minutes to make a homogeneous system. 10 mL of 86 mM cobalt(II) nitrate solution was further added to the above system in 30 minutes. The whole solution was further stirred for one hour and transferred into a Teflon lined stainless steel autoclave. The autoclave was sealed and maintained at 160 °C for 9 h. When the autoclave was cooled to ambient temperature, resulting precipitate was isolated by centrifugation and washed with hexane, pure water and ethanol for several times. Finally, the obtained product was dried in vacuum at 40 °C overnight and calcined in air at 300 °C for 3 hours.

The preparation of mesoporous CoO nanoplate is similar to that of mesoporous Co₃O₄ nanoplates except that the 300 °C calcination process is carried out under N₂ atmosphere for 3 hours.

3. Preparation of mesoporous Co₃M₂O₄ (M = Cu, Mn and Zn) nanoplates/nanosheets
To prepare mesoporous Cu₉O₂Co₂O₄ and MnCo₂O₄ nanoplates, similar procedures were employed as synthesizing mesoporous Co₃O₄ nanoplate. 10 mL of 86 mM cobalt(II) nitrate and 43 mM copper(II) nitrate or 43 mM manganese(II) nitrate solution were added to 25 mL homogeneous solution of urea, deionized water and ethanol including 4 mL oleic acid within 30 min. After sufficient stirring for one hour, the solution was transferred into a Teflon lined stainless steel autoclave, kept at the same parameters as that in preparation of Co₃O₄ nanoplates and then allowed for dry and calcination as described above.

The synthesis of mesoporous ZnCo₂O₄ nanosheets is carried out taking a similar method to the preparation of mesoporous Cu₉O₂Co₂O₄ and MnCo₂O₄, except that 86 mM cobalt(II) nitrate and 43 mM zinc(II) nitrate solution were added to the 25 mL reaction solution including 4 mL oleic acid.

4. Preparation of mesoporous CuO nanosheets
The preparation of mesoporous CuO was carried out as follows. 30 mL of tetrachloroethylen glycol and 30 mL of water were mixed together to make a homogeneous system. 0.6 g of urea and 5 mmol of copper(II) nitrate were then added to the above system and stirred for one hour to make a homogeneous solution. After that, the solution was transferred into a Teflon lined stainless steel autoclave, sealed and maintained at 120 °C for 12 h. When the reactor was cooled to room temperature, the products were readily obtained by sufficient washing by water and ethanol for several times and then allowed for drying at 40 °C in vacuum overnight. The CuO products were finally obtained by calcination of these obtained intermediates at 300 °C for 3 hours in air.

5. DFT calculations
DFT calculation details: density functional theory (DFT) calculation were carried out by using spin-polarized Kohn-Sham density functional theory (DFT). We used the generalized gradient approximation with the Perdew-Burke-Ernzerhof exchange-correlation functional as conducted in the Vienna ab initio simulation package (VASP). The valence orbitals of Co (3d, 4s), O (2s, 2p), C (2s, 2p), and H (1s) were described by plane-wave basis sets with cutoff energies of 400 eV. The Gaussian smearing method with a width of 0.20 eV was used. According to the experimental characterization results, Co₃O₄ with a space group of F-43m was used to model the catalyst structure. Bulk optimization yielded lattice parameters of a=b=c=8.065 Å. The periodic slab model of Co₃O₄ (110) was used to simulate the H₂O₂ decomposition reactivity. The Co₃O₄ (110) surface was modeled by p(2×2) four-atomic-layer supercells with the bottom two layers fixed, and the vacuum gap was set as 15 Å to avoid the interaction between the periodic images. Defective
Co$_3$O$_4$ (110) was constructed by deleting half a layer of Co and O atoms. All of the atoms in the structure were relaxed during the calculation. The Brillouin zone was sampled at $(2 \times 2 \times 1)$. The convergence criteria for the energy and force were set to $10^{-4}$ eV and 0.02 eV/Å. For evaluating the energy barriers, all transition states and pathways were computed using the climbing image nudged elastic band (CI-NEB) method. The adsorption energies were calculated according to the equation, $E_{\text{ads}} = E(\text{adsorbate/substrate}) - [E(\text{substrate}) + E(\text{adsorbate})]$, where $E(\text{adsorbate/substrate})$, $E(\text{adsorbate})$ and $E(\text{substrate})$ are energies of the substrate with the adsorbate, the gas-phase molecule and the clean substrate, respectively. The reaction energy and barrier were calculated by $E_r = E(\text{FS}) - E(\text{IS})$ and $E_a = E(\text{TS}) - E(\text{IS})$, where $E(\text{IS})$, $E(\text{FS})$ and $E(\text{TS})$ are the energies of the corresponding initial state (IS), final state (FS), and transition state (TS), respectively. Nudged elastic band (NEB) method that generally employed to investigate saddle points and minimum energy paths between reactants and products are conducted to reveal the energy barrier of O-O bond scission of ideal and defective Co$_3$O$_4$ (110).

6. Characterizations
The crystallographic structure of the obtained product was analyzed by powder X-ray diffraction (XRD, Bruker D8 Focus X-ray diffractometer, Cu Kα radiation, $\lambda = 0.1542$ nm). X-ray photoelectron spectroscopy (XPS) analysis was conducted on ESCALAB 250 Xi X-ray photoelectron spectrometer with Al Kα radiation. The specific surface area measurement was conducted on a Quantachromeautosorb IQ$_2$ instrument (Quantachrome Instruments). Compact secondary ion mass spectrometry (SIMS) was utilized to analyze the surface element composition of samples taking a dynamic mode. The ion beam and sputtering time is adjustable to optimize corresponding signals. Transmission electron microscopy (TEM) analysis and in-situ heating STEM was carried out on Talos F200X FEG TEM/STEM operating at 200 kV. Elemental mappings were collected with Super X system equipped with 4 Silicon Drift Detectors offering a total collection angle of 0.9 sr. The high-resolution STEM images were collected via Titan Themis 60-300 equipped with a Probe corrector to correct condenser lens aberration leading to 0.08 nm spatial resolution at 300 kV. The convergence angle is 25 mrad and HAADF STEM collection angle is 70–200 mrad. Electron tomography image series were acquired in HAADF-STEM mode with 10 mrad convergence angle and 30–200 mrad collection angle. The 3D volumes were reconstructed with IMOD software, visualized and analyzed with Avizo.
Figure S1. (a) and (b) SEM images of the prepared Cu$_2$(OH)$_2$CO$_3$ nanoplates. The average thickness of the Cu$_2$(OH)$_2$CO$_3$ nanoplates is measured to be 130±30 nm. (c) and (d) TEM images of the Cu$_2$(OH)$_2$CO$_3$ nanoplates. The Cu$_2$(OH)$_2$CO$_3$ nanoplates demonstrate a dog-bone-like morphology. (e) TEM image and (f) SEAD patterns of a Cu$_2$(OH)$_2$CO$_3$ nanoplate, which reveals the well-crystallized nature of the Cu$_2$(OH)$_2$CO$_3$ nanoplates. The inset of (a) is corresponding thickness distributions of Cu$_2$(OH)$_2$CO$_3$ nanoplates.
**Figure S2.** (a)-(c) Overall SEM images of the prepared Cu$_2$(OH)$_2$CO$_3$ nanoplates observed from low magnification to high magnification. (d) an enlarged SEM image of a Cu$_2$(OH)$_2$CO$_3$ nanoplate end, which shows the solid feature of the in line with the above TEM images in Figure S1. The insets of (b), (c), (d) are length, center width, and end width distributions of Cu$_2$(OH)$_2$CO$_3$ nanoplates, respectively. The average length of the Cu$_2$(OH)$_2$CO$_3$ nanoplates is measured to be 3.96±0.46 μm. The average center and end width of it are 0.85±0.12 μm and 1.05±0.17 μm, respectively.
Figure S3. (a) High-angle annular dark-field scanning TEM (HAADF-STEM) image of the mesoporous Co₃O₄ nanoplate. (b) Enlarged SEM image of cross-section of mesoporous Co₃O₄ nanoplate. The inset of (a) and (b) are length and thickness distributions of mesoporous Co₃O₄ nanoplates. The average length and thickness of mesoporous Co₃O₄ nanoplates are 3.88±0.24 μm and 90±20 nm, respectively.

Figure S4. FT-IR spectra of the Co₂(OH)₂CO₃ and Co₃O₄ nanoplates. In preparation, oleic acid was employed to direct the nanoplate morphology of Co₂(OH)₂CO₃. After calcination in air at 300 °C, the Co₂(OH)₂CO₃ was thermodynamically transformed to Co₃O₄ phase. Oleic acid was totally removed as evidenced by the disappearance of the oleic acid infrared absorption bands in the range of 1500-2000 cm⁻¹ and 2500-3000 cm⁻¹.¹
Figure S5. Pore size distributions of (a) mesoporous Co₃O₄ nanoplates and (b) Co₂(OH)₂CO₃ solid nanoplates.

Figure S6. XPS survey spectrum of the synthesized mesoporous Co₃O₄ nanoplates. All binding energy position was normalized taking the standard of C 1s with binding energy value of 284.6 eV. The XPS survey spectrum shows the sharp signal of Co 2p and O 1s signal as accorded with previous reports.²,³
Figure S7. XRD patterns of the synthesized Co(OH)$_2$ using NaOH as base sources. It was found that when NaOH was added to the synthetic system, Co(OH)$_2$ precipitates were immediately formed. XRD patterns of the precipitates agree well with the standard peaks of Co(OH)$_2$. The vertical lines in the pictures are the standard peaks of Co(OH)$_2$.

Figure S8. XRD patterns of the obtained CoCO$_3$ using Na$_2$CO$_3$ as base sources. Na$_2$CO$_3$ precipitates were immediately formed upon the addition of Na$_2$CO$_3$. However, the XRD patterns of Na$_2$CO$_3$ show a weak crystalline of it. The inset is the photo of Na$_2$CO$_3$ products.
Figure S9. (a) XRD patterns of the control sample using pure water as solvent in preparation. The vertical lines represent the standard peaks of Co(CO$_3$)$_{0.5}$(OH)$_{0.11}$H$_2$O (PDF No. 48-0083). (b) The picture of the Co(CO$_3$)$_{0.5}$(OH)$_{0.11}$H$_2$O powders. (c) and (d) TEM images of the prepared Co-based basic carbonate (Co(CO$_3$)$_{0.5}$(OH)$_{0.11}$H$_2$O).

Figure S10. (a) XRD patterns of the control sample prepared by taking pure ethanol as solvent. The vertical lines represent the standard peaks of Co$_2$(OH)$_2$CO$_3$ (PDF No. 01-079-7085). (b) The picture of the Co$_2$(OH)$_2$CO$_3$ powders. (c) and (d) TEM images of the prepared Co-based basic carbonate (Co$_2$(OH)$_2$CO$_3$).
Figure S11. (a) XRD patterns of the control sample prepared by employing mixed solvent of ethanol and water (the volume ratio of ethanol to water is 3:4) in the absence of oleic acid. The vertical lines represent the standard peaks of Co$_3$O$_4$ (PDF No. 43-1003). (b) The picture of the Co$_3$O$_4$ powders. (c) and (d) TEM images of the prepared Co$_3$O$_4$.

Figure S12. (a) XRD patterns of the prepared control sample using 0.17 mM oleic acid in preparation. (b)-(d) corresponding TEM images of the control sample.
Figure S13. (a) XRD patterns of the prepared control sample using 0.46 mM oleic acid in preparation. (b)-(d) corresponding TEM images of the control sample.

Figure S14. SEM images of the prepared Cu$_2$(OH)$_2$CO$_3$ solid nanoplates prepared with (a) 0.17 M oleic acid and (b) 0.46 M oleic acid.
**Figure S15.** (a) XRD patterns of the cobalt hydroxide carbonate nanoplate calcined at 150 °C. (b)-(d) are corresponding TEM images of the calcined (treated at 150 °C) cobalt hydroxide carbonate nanoplate. It is demonstrated that after 150 °C calcination, the cobalt hydroxide carbonate nanoplates remain stable without pore formation or phase transformation to Co$_3$O$_4$.

**Figure S16.** (a) XRD patterns of the cobalt hydroxide carbonate nanoplate calcined at 550 °C for 3 h. After calcination, the cobalt hydroxide carbonate well transforms to Co$_3$O$_4$. The vertical lines are the standard peaks of Co$_3$O$_4$. (b)-(d) are TEM images of the formed mesoporous Co$_3$O$_4$ nanoplate. Enlarged TEM images in (b) show that the mesopores of the Co$_3$O$_4$ nanoplate are around 43 nm with a wide size distribution (43±14 nm). The inset of (b) is the corresponding pore size distributions.
Figure S17. (a) and (b): SEM images of the mesoporous CoO nanoplates. (c) and (d): Representative TEM images of the synthesized mesoporous CoO nanoplates. (e) Enlarged TEM image of a mesoporous CoO nanoplate. The inset of (e) is corresponding SEAD patterns of a mesoporous CoO nanoplate, demonstrating well-crystallized nature of it. (f) Enlarged TEM picture of a CoO nanoplate end, which shows the well-defined mesoporous structures.
Figure S18. (a) and (b): SEM images of the mesoporous Cu$_{0.92}$Co$_{2.08}$O$_4$ nanoplates. (c)-(e): Representative TEM images of the synthesized mesoporous Cu$_{0.92}$Co$_{2.08}$O$_4$ nanoplates. (f) Enlarged TEM image of a mesoporous Cu$_{0.92}$Co$_{2.08}$O$_4$ nanoplate that show the mesoporous nature of Cu$_{0.92}$Co$_{2.08}$O$_4$ nanoplates, which is further demonstrated in (h). (g) is SEAD patterns of a mesoporous Cu$_{0.92}$Co$_{2.08}$O$_4$ nanoplate, which reveals good crystalline of it.
Figure S19. (a) SEM image of the prepared mesoporous MnCo$_2$O$_{4.5}$ nanoparticles. (b), (c) and (d) Representative TEM images of the obtained mesoporous MnCo$_2$O$_{4.5}$ nanoparticles. (e) SEAD patterns of a mesoporous MnCo$_2$O$_{4.5}$ nanoplate. The well-defined patterns show high crystalline nature of the mesoporous MnCo$_2$O$_{4.5}$ nanoplates. (f) Enlarged TEM picture of a CoO mesoporous MnCo$_2$O$_{4.5}$ nanoplate end, which obviously demonstrates the mesoporous structures.
Figure S20. (a) SEM image of the mesoporous ZnCo$_2$O$_4$ nanoplates. (b) and (c) Representative TEM images of the synthesized mesoporous ZnCo$_2$O$_4$ nanoplates. The inset of (c) is corresponding SEAD patterns of the mesoporous ZnCo$_2$O$_4$ nanoplate. The ordered patterns reveal high crystalized mesoporous ZnCo$_2$O$_4$ nanoplates. (d) is the enlarged TEM picture of local end of the mesoporous ZnCo$_2$O$_4$ nanoplate, which shows well-defined mesoporous structures.
**Figure S21.** (a) SEM images and corresponding EDS elementary mapping images of (a) mesoporous CoO nanoplates, (b) mesoporous Cu$_{0.92}$Co$_{2.08}$O$_4$ nanoplates, (c) mesoporous MnCo$_2$O$_{4.5}$ nanoplates, (d) mesoporous ZnCo$_2$O$_4$ nanosheets.
Figure S22. (a) XRD patterns of the prepared Cu$_2$(OH)$_2$CO$_3$ (PDF No. 41-1390). (a) XRD patterns of mesoporous CuO (PDF No. 44-0706). (c) and (d) are the TEM images of solid Cu$_2$(OH)$_2$CO$_3$ nanoplate and mesoporous CuO nanosheet. The vertical lines of (a) and (b) are standard peaks of Cu$_2$(OH)$_2$CO$_3$ and CuO respectively.

The void ratio from BET measurement is based on the following equation:

\[ R_{void} = \frac{V_m}{\frac{1}{p} + V_m} \]

Where \( p \) is the density of Co$_3$O$_4$ nanoparticles (6.11 g/cm$^3$) and \( V_m \) is the pore volume from BET measurements (0.15 cm$^3$/g). \( R_{void} \) is the void ratio of mesoporous Co$_3$O$_4$ nanoplate.

By the above calculation, the void ratio of the mesoporous Co$_3$O$_4$ nanoplate is determined as 48.3%.
Figure S23. Aberration-corrected HAADF-STEM images of the prepared mesoporous Co$_3$O$_4$ nanoplates. The red arrows show the defective cation sites on the surface of mesoporous Co$_3$O$_4$ nanoplates.

Figure S24. (a)-(c) Atomic HAADF-STEM images of the mesoporous Co$_3$O$_4$ nanoparticles and their surface with atomic steps and high-index terminations.
Figure S25. (a) and (b) High-angle annular dark field scanning transmission electron microscopy images of commercial Co$_3$O$_4$ nanoparticles. (c) and (d) Enlarged aberration-corrected transmission electron microscopy images of commercial Co$_3$O$_4$, which reveals the perfect crystalline surface of it.

Figure S26. (a) Oxygen evolution volume as a function of time over the mesoporous Co$_3$O$_4$ catalysts. (b) TEM image of the prepared the mesoporous Co$_3$O$_4$ catalysts according to reference.$^4$
Figure S27. (a) Absorbance variation over Co$_3$O$_4$ nanocatalysts as a function of reaction time measured at 652 nm wavelength. (b) Measurements of the mesoporous Co$_3$O$_4$ nanoplate concentration effect on chemical transformation rate of TMB in the presence of H$_2$O$_2$. The reaction system includes 0.25 mM TMB, 50 mM H$_2$O$_2$, and varied Co$_3$O$_4$ concentrations in 3 mL sodium acetate buffer (pH = 5).

Figure S28. (a) The atomic model of ideal Co$_3$O$_4$ (110). (b) The atomic model of defective Co$_3$O$_4$ (110) with steps.
Figure S29. Wulff construction of Co$_3$O$_4$ nanoparticles in the skeleton of mesoporous Co$_3$O$_4$ nanoplates.

\begin{align*}
(1) \quad & \text{H}_2\text{O}_2 + \ast \leftrightarrow \text{H}_2\text{O}_2^* \\
(2) \quad & \text{H}_2\text{O}_2^* + \ast \leftrightarrow \text{OH}^* + \text{OH}^* \quad \text{O-O bond scission} \\
(3) \quad & \text{OH}^* + \text{OH}^* \leftrightarrow \text{O}^* + \text{H}_2\text{O}^* \\
(4) \quad & \text{O}^* + \text{O}^* \leftrightarrow \text{O}_2^* \quad \text{O}^*+\text{O}^* \text{ recombination} \\
(5) \quad & \text{O}_2^* \leftrightarrow \text{O}_2 + \ast \\
\end{align*}

Figure S30. The overall reaction pathways of H$_2$O$_2$ over ideal and defective Co$_3$O$_4$ (110).
Figure S31. $\text{H}_2\text{O}_2$ adsorption on defective $\text{Co}_3\text{O}_4$ (110) with top and cross view.
Table S1. Comparison of BET surface areas of mesoporous Co$_3$O$_4$ nanoplates and other reported mesoporous Co$_3$O$_4$.

<table>
<thead>
<tr>
<th>Entry</th>
<th>BET surface area (m$^2$/g)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mesoporous Co$_3$O$_4$ nanoplates</td>
<td>127</td>
<td>Current work</td>
</tr>
<tr>
<td>Meso-Co-350</td>
<td>121</td>
<td>Chem. Mater. 2014, 26, 4629–4639</td>
</tr>
<tr>
<td>Co$_3$O$_4$-100</td>
<td>113</td>
<td>Nano Res. 2013, 6, 47-54.</td>
</tr>
<tr>
<td>Meso-Co$_3$O$_4$</td>
<td>104</td>
<td>Appl. Catal., B 2016, 180, 139-149.</td>
</tr>
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</table>

Table S2. The surface Co:O ratio of mesoporous Co$_3$O$_4$ nanoplates and commercial Co$_3$O$_4$ determined by the secondary ion mass spectrometry (SIMS) characterizations.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Co:O ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mesoporous Co$_3$O$_4$ nanoplates</td>
<td>0.18:1</td>
</tr>
<tr>
<td>Commercial Co$_3$O$_4$ nanoparticles</td>
<td>0.38:1</td>
</tr>
</tbody>
</table>

During secondary ion mass spectrometry (SIMS) measurements, the sputtering depth is 0.5 nm. The commercial Co$_3$O$_4$ nanoparticles afford perfect crystalline surface without obvious surface cation defect. By rational comparison of Co to O ratio between commercial Co$_3$O$_4$ nanoparticles and our mesoporous Co$_3$O$_4$ nanoplates, there are obvious cation missing on the surface of mesoporous Co$_3$O$_4$ nanoplates.

Table S3. Comparison of H$_2$O$_2$ decomposition activity over mesoporous Co$_3$O$_4$ nanoplates and other Co$_3$O$_4$-based catalysts. K is the first order rate constant. R is K to specific surface area of catalyst.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Turnover frequency (min$^{-1}$)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mesoporous Co$_3$O$_4$ nanoplates</td>
<td>31.3</td>
<td>Current work</td>
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<tr>
<td>Commercial Co$_3$O$_4$</td>
<td>3.13</td>
<td>Current work</td>
</tr>
<tr>
<td>Mesoporous Co$_3$O$_4$</td>
<td>0.26</td>
<td>Current work</td>
</tr>
<tr>
<td>0.1 CoZnO$_{1.33}$-500</td>
<td>~1.15</td>
<td>Mater. Chem. Phys. 2017, 185, 44-54.</td>
</tr>
<tr>
<td>Co$_3$O$_4$-H$_2$O$_2$</td>
<td>2.79</td>
<td>Cryst. Growth Des. 2016, 16, 6286-6293</td>
</tr>
</tbody>
</table>
References