The electrocatalytic oxygen evolution reaction (OER) is important to energy conversion and storage applications, such as water splitting and metal-air batteries.\cite{1-3} While RuO$_2$ has been regarded as the benchmark OER catalyst due to its superior performance\cite{4-6}, its scarcity and high cost prohibit the large-scale applications. As such, exploiting earth-abundant and low-cost OER electrocatalysts with high catalytic performance has attracted great attentions\cite{7-13}. The available scientific evidence has shown that the spinel-type binary metal oxides, such as CoFe$_2$O$_4$\cite{14}, NiCo$_2$O$_4$\cite{15, 16}, ZnCo$_2$O$_4$\cite{17}, Cu$_x$Co$_{3-x}$O$_4$\cite{18}, and Li$_x$Co$_{3-x}$O$_4$\cite{18}, could be a class of promising candidates due to their superior chemical stability and catalytic activity\cite{19}. However, they have drawbacks such as inferior electrical conductivity\cite{20} and low concentration of catalytic active sites.
A number of recent reports suggest that anchoring nano-sized electrocatalysts onto conductive porous and high-surface area supports (e.g., active carbon, carbon nanotubes, and graphene) could be used to noticeably increase the electrical conductivity and catalytic active sites, leading to an enhanced OER performance.\[21-30\]

In previous studies, the anchoring of oxides is generally implemented through physical mixing of metal salts and carbon precursors followed by additional thermal treatments.\[27, 31, 32\] Nevertheless, the catalysts synthesized via such approaches possess unsatisfactory performance due to the incomplete conversion of binary metal oxide or highly resistive heterogeneous contacts.\[33\] To this end, the concurrent growth of strongly coupled binary metal oxides and conductive carbon materials could be an effective means to overcome the aforementioned problems.\[34, 35\] This is because that the formation of nanostructured carbon under the concurrent growth conditions can spatially confine the growth of metal oxide nanocrystals,\[34\] giving a rise on the synergistic interaction between the binary metal oxide and carbon in the nanocomposite to improve density of catalytic active sites and electrical conductivities, favourable for electrocatalytic OER.

Herein, we report a molten-salt calcination method to concurrently grow a spinel-type of CoCr\(_2\)O\(_4\)/carbon nanosheets (CoCr\(_2\)O\(_4\)/CNS) composite from the metal oleate complex precursors, as schematically illustrated in Figure 1. The sample resulting from 700 °C treatment (CoCr\(_2\)O\(_4\)/CNS-700, the affiliated number annotates the treatment temperature of samples) displays a superior OER catalytic performance than the benchmark commercial RuO\(_2\) electrocatalyst in 1.0 M KOH electrolyte with low overpotential and Tafel slope of 326 mV (at the current density of 10 mA cm\(^{-2}\)) and 51.0 mV dec\(^{-1}\), respectively.

In a typical synthetic process, the metal oleate (CoCr\(_2\)(OH)\(_x\)/OA) precursor (obtained by complexion of metal salts and sodium oleate, see Experimental Section, Supporting Information) is calcined with the molten-salt (Na\(_2\)SO\(_4\)) under Ar atmosphere. The X-ray diffraction (XRD) pattern (Figure 2a) of the as-synthesized CoCr\(_2\)O\(_4\)/CNS-700 product can be indexed as the cubic spinel phase of CoCr\(_2\)O\(_4\) crystal structure (JCPDS 80-1668).\[36, 37\] In
addition, the Raman spectrum of CoCr$_2$O$_4$/CNS-700 (Figure 2b) displays the pure CoCr$_2$O$_4$ characteristic bands peaked at 189 ($F_{2g}$), 458 ($E_g$), 517 ($F_{2g}$) and 667 cm$^{-1}$ ($A_{1g}$), which also support the formation of the cubic spinel phase of CoCr$_2$O$_4$.\cite{38} Interestingly, no obvious carbon diffraction peak in XRD pattern (Figure 2a) can be identified, implying that the carbon is not in the pure graphitic form.\cite{39} The Raman spectrum (Inset in Figure 2b) demonstrates the carbon nanosheets (CNS) as disordered graphitic carbon are formed by the observed bands at 1336 cm$^{-1}$ (D) and 1601 cm$^{-1}$ (G).\cite{34,40}

Figure 2c shows a typical scanning electron microscopic (SEM) image of the as-synthesized CoCr$_2$O$_4$/CNS-700 sample, revealing an irregular petal-like morphology. The selected area electron diffraction (SAED) pattern (bottom inset in Figure 2d) confirms the existence of (111), (222), (400), (440) and (533) planes, which are consistent with the XRD results shown in Figure 2a. The HRTEM image (top inset in Figure 2d) shows a lattice spacing of 0.48 nm, corresponding to the (111) plane of the cubic spinel structured CoCr$_2$O$_4$. Furthermore, the high resolution transmission electron microscopic (HRTEM) image (Figure 2d) confirms that the irregular petal-like nanostructures are formed by CoCr$_2$O$_4$ nanoparticles (sized from 5-15 nm) embedded on CNS. Such a CoCr$_2$O$_4$/CNS hybrid structure could lead to a sophisticated connectivity between the nanostructured CoCr$_2$O$_4$ and conductive CNS, facilitating OER charge transfer process.

To understand the coupling effect on the interface properties of CoCr$_2$O$_4$/CNS catalysts, X-ray photoelectron spectroscopic (XPS) measurements are conducted. The survey spectrum reveals the presence of C, O, Cr and Co (Figure S2). For a meaningful comparison, pure nanoparticulate CoCr$_2$O$_4$ (denoted as CoCr$_2$O$_4$-700) is synthesized at 700 °C using the same experimental procedure without carbon source. The high resolution Co 2p (Figure S3) and Cr 2p spectra (Figure S4) of CoCr$_2$O$_4$/CNS-700 and CoCr$_2$O$_4$-700 are similar, which can be assigned as the states of divalent Co and trivalent Cr species, respectively.\cite{33,36,41,42} However, the surface oxygen states of the two samples are much different. The deconvoluted O 1s XPS spectra of CoCr$_2$O$_4$/CNS-700 and CoCr$_2$O$_4$-700 display three peaks at 530.7 (O3), 532.1 (O2) and 533.2 (O1) eV, respectively (Figure
2e, f). The fitted O3 peak is associated with the lattice oxygen atoms with saturated coordination number 3. The O2 peak can be related to the oxygen atoms possessing low coordination numbers 2 or 1 and O1 peak stands for the oxygen atoms from hydroxyl species of surface-adsorbed water molecules. The larger O2 peak area in CoCr$_2$O$_4$/CNS-700 compared to CoCr$_2$O$_4$-700 reveals the higher concentration of low-coordinated surface O atoms in CoCr$_2$O$_4$/CNS-700 sample, which demonstrates that the strong coupling between CoCr$_2$O$_4$ nanocrystals and CNS can chemically affect the interface properties and preserve low-coordinated surface O atoms to a higher extent in the nanocomposite during high temperature calcination under Ar atmosphere.

The electrocatalytic OER performances of the CoCr$_2$O$_4$/CNS nanocomposites are appraised in 0.1 M and 1.0 M KOH electrolytes using a standard three-electrode system, respectively (Supporting Information). Figure 3a, b show the polarization curves of CoCr$_2$O$_4$/CNS-700, CoCr$_2$O$_4$-700 and commercial RuO$_2$ electrocatalysts obtained under a scan rate of 5 mV s$^{-1}$. For 0.1 M KOH electrolyte, a sharp increase in anodic current at an onset potential of $\sim$1.47 V (vs. RHE) is observed for both CoCr$_2$O$_4$/CNS-700 and commercial RuO$_2$ electrodes, whereas a significantly anodic shifted onset potential ($\sim$1.52 V) is observed from the CoCr$_2$O$_4$-700 electrode. Almost identical onset potentials of CoCr$_2$O$_4$/CNS-700 and commercial RuO$_2$ electrocatalysts indicate superior intrinsic catalytic activity of CoCr$_2$O$_4$/CNS-700 toward OER. At a current density of 10 mA cm$^{-2}$, the observed OER overpotential at CoCr$_2$O$_4$/CNS-700 electrode is 365 mV, which is even 9 mV lower than that of commercial RuO$_2$ electrode (374 mV) and significantly lower than that of CoCr$_2$O$_4$-700 (Figure 3a), indicating the importance of CNS in enhancing the electrocatalytic OER performance of the catalyst. Similar results are also observed when 1.0 M KOH is used as the electrolyte (Figure 3b). The observed OER overpotential at CoCr$_2$O$_4$/CNS-700 electrode under a current density of 10 mA cm$^{-2}$ is 326 mV, which is 10 mV and 96 mV lower than that of commercial RuO$_2$ and CoCr$_2$O$_4$-700 electrocatalysts, respectively. Furthermore, the OER overpotentials at CoCr$_2$O$_4$/CNS-700 electrode under a
current density of 10 mA cm\(^{-2}\) in both 0.1 M and 1.0 M KOH electrolytes are superior than the vast majority of widely reported spinel-type binary metal oxide electrocatalysts (Table S1, Supporting Information).

The electrocatalytic kinetics of CoCr\(_2\)O\(_4\)/CNS-700, CoCr\(_2\)O\(_4\)-700 and commercial RuO\(_2\) electrodes toward OERs in 0.1 M and 1.0 M KOH electrolytes are evaluated by the Tafel polarization method at a scan rate of 1 mV s\(^{-1}\), as shown in Figure 3c, d. With 0.1 M KOH electrolyte, the Tafel slope values of 58.2, 79.9 and 65.0 mV dec\(^{-1}\) are obtained for CoCr\(_2\)O\(_4\)/CNS-700, CoCr\(_2\)O\(_4\)-700 and commercial RuO\(_2\) electrocatalysts, respectively (Figure 3c). Whereas, the corresponding Tafel slope values obtained from CoCr\(_2\)O\(_4\)/CNS-700, CoCr\(_2\)O\(_4\)-700 and commercial RuO\(_2\) in 1.0 M KOH are respectively decreased to 51.0, 63.3 and 52.9 mV dec\(^{-1}\) (Figure 3d). Also, the calculated turnover frequency (TOF) and mass activity of CoCr\(_2\)O\(_4\)/CNS-700 are found to be 0.0314 s\(^{-1}\) and 53.41 A g\(^{-1}\), are much higher than those of CoCr\(_2\)O\(_4\)-700 and RuO\(_2\) (Table S2, Supporting Information) electrocatalysts. These results further confirm the superior electrocatalytic OER kinetics of CoCr\(_2\)O\(_4\)/CNS-700 electrode.

To understand the origin of the superior OER kinetics, the electrocatalytic charge transfer resistance of CoCr\(_2\)O\(_4\)/CNS-700, CoCr\(_2\)O\(_4\)-700 and commercial RuO\(_2\) are characterized by the electrochemical impedance spectroscopy (EIS) technique (Figure 3e). The obtained Nyquist plot of CoCr\(_2\)O\(_4\)/CNS-700 electrode exhibits a charge transfer resistance (R\(_{ct}\)) of 12.6 Ω, the lowest among CoCr\(_2\)O\(_4\)-700 (37.7 Ω) and commercial RuO\(_2\) (15.8 Ω) electrodes. It demonstrates that the strong coupling between the CrCo\(_2\)O\(_4\) nanoparticles and CNS in the CoCr\(_2\)O\(_4\)/CNS-700 sample can benefit the charge transfer process and further improve the electrical conductivity and OER kinetics.

The electrocatalytic stability of CoCr\(_2\)O\(_4\)/CNS is also examined by the chronopotentiometric method under a constant current density of 10 mA cm\(^{-2}\) (Supporting Information). As shown in Figure 3f, the CoCr\(_2\)O\(_4\)/CNS-700 well retains its electrocatalytic activity over the testing period (10000 s) with an insignificant increase in the overpotential (<60 mV) compared to CoCr\(_2\)O\(_4\)-700
(~180 mV). It suggests the coupling in CrCo$_2$O$_4$/CNS can also improve the stability of catalyst. In strong contrast, the operating overpotential of RuO$_2$ increases rapidly within 3600s (~190 mV) under the same experimental condition. Based on the above merits, the CoCr$_2$O$_4$/CNS-700 nanocomposite can afford high catalytic efficiency and durability than that of the benchmark RuO$_2$ catalyst.

To shed light on the high performance of CoCr$_2$O$_4$/CNS for OERs, first-principles density functional theory (DFT) studies with the consideration of spin-polarization are performed. According to the O 1s XPS spectra (Figure 2e, f) of CoCr$_2$O$_4$/CNS-700 and CoCr$_2$O$_4$-700, the concentration of low-coordinated surface O2 atoms is greatly affected by the coupling of CoCr$_2$O$_4$ and CNS. As such, the different OER performances between CoCr$_2$O$_4$/CNS-700 and CoCr$_2$O$_4$-700 should mainly be ascribed to O2 atoms. Herein, the atomistic CoCr$_2$O$_4$ (111) surface models with or without low-coordinated O2 atoms (Figure 4a, b) are employed to investigate the water adsorption properties since the water adsorption is an essential process for the electrocatalytic OER.$^{[16]}$ Our DFT calculation results suggest that the adsorption energy of water on the surface with O2 atoms is -0.74 eV, which is 27.0% lower than that on the surface without O2 atoms (-0.54 eV). The lower adsorption energy means a stronger interaction between water molecule and the surface with O2 atoms. After the structural optimization, the H atoms of water point towards two surface O2 atoms with the distances of 2.26 and 2.36 Å, respectively (Figure 4c). Such short distances manifest the formation of hydrogen bonding, which can stabilize the adsorbed water molecule. However, similar hydrogen bonding cannot be formed on the surface without O2 atoms (Figure 4d). As a result, the surface metals associated with surface O2 atoms are the active sites, which can promote the interaction between water molecule and catalysts, benefiting the electrocatalytic OERs. Given that the low-coordinated O2 atoms can only be largely preserved $via$ the strong coupling of CNS in the CoCr$_2$O$_4$/CNS-700 catalyst (Figure 2e, f), it
explains the superior electrocatalytic OER performance of CoCr$_2$O$_4$/CNS-700 due to the higher concentration of these catalytic active sites.

In summary, the strongly coupled CoCr$_2$O$_4$/CNS nanocomposite is concurrently grown by using a facile one-step molten-salt calcination method. Compared with the pure CoCr$_2$O$_4$, the catalyst coupled with CNS exhibits better electrocatalytic activity, good durability, lower overpotential at current density of 10 mA cm$^{-2}$ and smaller Tafel slope. This is because the interaction between CoCr$_2$O$_4$ nanoparticles and CNS can increase the electrical conductivities and the concentration of catalytic active sites. Moreover, the performance of the strongly coupled CoCr$_2$O$_4$/CNS nanocomposite is even better than the benchmark RuO$_2$ electrocatalyst and other reported spinel type binary metal oxide electrocatalysts, which paves the way to use earth-abundant electrocatalysts for OERs. The synthetic approach used in this work can also be further explored to fabricate other metal oxides/carbon nanosheets composite via the same one-step concurrent growth manner for energy conversion and storage applications.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Figure 1. Schematic illustration of the molten-salt concurrent growth approach.

Figure 2. (a) XRD pattern (*indicating Na$_2$SO$_4$ peaks); (b) Raman spectra; (c) SEM image; (d) HRTEM and local HRTEM images (Top inset) and SAED pattern (Bottom inset); O 1s XPS spectra of (e) CoCr$_2$O$_4$/CNS-700 and (f) CoCr$_2$O$_4$-700. The red and yellow arrows in (d) indicate CNS and CoCr$_2$O$_4$ nanocrystals, respectively.

Figure 3. Polarization curves (a, b) and Tafel plots (c, d) of CoCr$_2$O$_4$/CNS-700, CoCr$_2$O$_4$-700 and RuO$_2$ in 0.1 and 1.0 M KOH electrolyte; (e) Nyquist plots of CoCr$_2$O$_4$/CNS-700, CoCr$_2$O$_4$-700 and RuO$_2$ at an overpotential of 340 mV in 1.0 M KOH; (f) chronopotentiometric measurement of OER by CoCr$_2$O$_4$/CNS-700, CoCr$_2$O$_4$-700 and RuO$_2$ catalyst at a current density of 10 mA cm$^{-2}$ in 1.0 M KOH.

Figure 4. Optimized atomic configurations of the CrCr$_2$O$_4$ (111) surface (a) with and (b) without low-coordinated surface O2 atoms; and the relevant atomic configurations after H$_2$O adsorption on the CrCr$_2$O$_4$ (111) surface (c) with and (d) without low-coordinated surface O2 atoms, respectively. Key: blue-Co, Cyan-Cr, red-O and light pink-H.
Figure 1

Before Calcination

After

:Na$_2$SO$_4$ :CoCr$_2$O$_4$/CNS :CoCr$_2$(OH)$_x$/OA

Figure 2

JCPDS No# 80-1668

(a) JCPDS No# 80-1668

(b) Wavenumber (cm$^{-1}$)

(c) Intensity (a.u.)

(d) Wavenumber (cm$^{-1}$)

(e) Intensity (a.u.)

(f) Intensity (a.u.)
Figure 3

Figure 4