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Nanoclay-modulated oxygen vacancies of metal oxide

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The formation of oxygen vacancies is one of the most critical factors that can improve the electronic and catalytic properties of metal oxides, in which an important challenge is to lower the formation energy of oxygen vacancies at the interface structure. Here we show that clay surfaces rich with hydroxyl groups can induce the formation of oxygen vacancies in metal oxide catalysts. Based on density functional theory calculations, kaolinite is shown to hinder the surface dehydration process of Co_3O_4 nanoparticles, and enhances the charge transfer process at the interface by the highly diffusible protons. Experimental results confirm that vacancy-rich Co_3O_4 is easily produced by a reduction method and kaolinite enhances the formation of oxygen vacancies and divalent cobalt on the nanoparticle surface. As expected, the defective Co_3O_4 /kaolinite exhibits enhanced catalytic and electrocatalytic performances. This finding provides an improved way to design efficient clay-based catalysts.

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The presence of several oxygen vacancies (V_O) is of great importance for nanocomposites to be used in nanomaterials.^{1–3} The electronic structure and catalytic properties of metal oxides (MO) can be tuned by introducing defect sites such as a vacancy and heteroatom, which manipulate their donor densities in transition metal oxides^{4–6}. In catalytic systems, intrinsic structural defects can distinctly enhance the catalytic activity of nanocrystals^{7–9}. Motivated by the advantages for oxygen vacancies, many researchers have focused on the development of new methods and approaches to generate appropriate density of defects on nanocrystals^{10–12}. Owing to its low-cost, outstanding redox capability and favorable electrical conductivity, Co_3O_4 represents a promising candidate in various fields, including water splitting¹³, lithium-ion battery¹⁴, and particularly the field of heterogeneous catalysis^{15,16}. In addition, the specific crystal structure of spinel Co_3O_4 with tetrahedral Co^{2+} ions and octahedral Co^{3+} ions have excellent environmental stability¹⁷. In some of the previous studies, oxygen vacancies were introduced into MO by an efficient Ar plasma strategy or a simple heat treatment to achieve enhanced electrocatalytic reduction^{18–20}. As a reductant, NaBH_4 was used to produce oxygen vacancies on the surface of reducible MO, which provide more active sites for oxygen evolution reaction catalysis²¹. Normally, the amount of oxygen vacancies would be

increased by increasing the concentration of NaBH_4 . Tailoring oxygen vacancy of transition MO in the interface still remains a challenge.

Currently, clay minerals are considered as promising supporting materials with uniform morphology and environmental friendly properties^{22,23}. Kaolinite (Kaol), a silicate mineral with chemical composition of $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$, is a typical 1:1 layered material with high crystallinity and special surface properties formed by stacking Al–O octahedral and Si–O tetrahedral structure^{24,25}. Specifically, a pivotal intrinsic surface property on kaolinite is the existence of plenty of hydroxyl groups, which are beneficial for catalytic reactions^{26,27}. This clay mineral has been widely applied to assemble functional nanoparticles due to its special surface properties, such as highly hydrophilic surface, large surface area and high stability.

Here, we report density functional theory (DFT) calculations on the interface structure and reduction properties of MO/clay interface, and propose a rational design of Co_3O_4 /kaolinite (Co_3O_4 /Kaol) composite catalyst for oxidation of pollutants. V_O -rich Co_3O_4 /Kaol composites with ultrafine-sized Co_3O_4 anchored on clay surface are synthesized by the reduction method. In addition, the $\text{Co}^{2+}/\text{Co}^{3+}$ redox behavior could also contribute to the high-catalytic activity. It is found that the Al–OH hydroxyl groups on kaolinite surface play a pivotal role in modulating the

Fig. 1 Atomic structure evolution and charge transfer of Co_3O_4 /kaolinite interface. Illustration of the support effect of clay on the atomic structure and energetics of MO (Co_3O_4 in this case) during the adsorption, calcination, and reduction processes, based on DFT calculations. During the adsorption of Co_3O_4 clusters on kaolinite, the strong interface bonding leads to the partial reduction of Co^{3+} ($\text{Co}(\text{OH})^{3+} \rightarrow \text{Co}(\text{OH})^{3-}$) due to the charge transfer (h^+) and dispersion force between Co_3O_4 and kaolinite surface. The partial dehydration of Co_3O_4 occurs when calcined at the temperature where full dehydration should occur, due to surface distortion and bond shrink of Co_3O_4 ($\text{Co}(\text{OH})^{3-} \rightarrow \text{Co}(\text{V})^{3-}$) when supported on kaolinite. The V_O formation energy of Co_3O_4 decreased significantly under the charge compensation of protons (H^+) from the hydroxyl groups retained by clay surface, as predicted by DFT calculations. And low spin (LS) Co^{3-} reduced to high spin (HS) Co^{2+} . Dehydration energy and V_O formation energy of Co_3O_4 with and without kaolinite support are given in Supplementary Figures 2 and 3. The support effect of kaolinite leads to the easier formation of V_O on Co_3O_4 /kaolinite interface.

Fig. 2 Atomic structure and electronic structure of Co_3O_4 /Kaolinite interfaces. **a** Charge density difference of Co_3O_4 /kaolinite and **b** $\text{R-Co}_3\text{O}_4$ /kaolinite. Blue corresponds to charge depletion and red to charge gain. Isosurfaces are shown in the range $[-0.08$ to $0.08]$ ($\text{e}/\text{\AA}^3$). **c** The top view of $\text{R-Co}_3\text{O}_4$ /kaolinite. The partial density of states (PDOSs) of **d** Co_3O_4 cluster, **e** Co_3O_4 /kaolinite interface, and **f** $\text{R-Co}_3\text{O}_4$ /kaolinite interface. The PDOSs of Co_3O_4 in the last two structures are highlighted by gray area

amount of oxygen vacancy and Co^{2+} on Co_3O_4 surface, and thus improving electronic structure and catalytic performance of Co_3O_4 . The clay-supported oxide catalyst is clarified by a rational relationship between clay-modulated active sites and the enhanced catalytic activity, which could shed some light on future design of clay-supported catalysts.

Results

Support effect on the formation of oxygen vacancies. Although clay minerals have been used as support materials during the past decades to load various functional particles for adsorption and catalytic applications, however, no detailed mechanism at atomic level was revealed so far. The reactions at the mineral–aqueous solution interface have attracted much attention during recent years²⁸. Theoretical descriptions of interface structures between kaolinite and supported transition MO are still open questions due to several factors, such as the cluster structures of transition oxide, the charge and spin of TM ions, adsorption configurations, the influence of water molecules, and the diffusion of hydrogen atoms.

Based on DFT calculations, we have explored three typical processes involved in the synthesis of clay-supported oxides, i.e., adsorption, calcination, and reduction processes (Fig. 1). The interfacial structure is rather complicated since the Co–OH groups at Co_3O_4 cluster surface and the Al–OH groups at kaolinite surface are distorted under the influence of dispersion force (including hydrogen bonding) and interface charge transfer during the adsorption and calcination processes. During the adsorption process at Co_3O_4 /Kaol interface, the adsorption energy is influenced by the distribution and specific contact configuration of Co_3O_4 nanocluster on kaolinite surface, such as spatial rotation (Supplementary Figure 1a) and translation at vertical and horizontal space (Supplementary Figure 1b). It is demonstrated that the hydrated Co_3O_4 nanoclusters can be

strongly bonded to the entire surface of kaolinite, although the adsorption energy varies from -1.0 to -3.0 eV upon the spatial distribution of Co_3O_4 cluster on kaolinite surface, as influenced by interface bonding and structure distortions. The configurations with lowest adsorption energy come from configurations with most of their hydroxyl groups of Co_3O_4 closely adhered on kaolinite surface. Slight distortion of hydroxyl groups on Co_3O_4 cluster and kaolinite surface were identified as the main cause, due to the charge transfer at Co_3O_4 /kaolinite interface (Fig. 2a). Occasionally, diffusions of one or two H atoms, i.e., redistribution of H bonding network on Co_3O_4 will lower the energy by ~ 0.5 eV. The calculated adsorption energies of Co_3O_4 cluster on kaolinite surface (Supplementary Figure 1c) are much lower than that of Co_3O_4 cluster on graphene (-0.88 eV)²⁹, which is mainly attributed to the higher hydrophilic surface of clay mineral compared to other widely studied support materials.

The adsorption energy (E_{ads}) of Co_3O_4 clusters on the surface of kaolinite is calculated as $E_{\text{ads}} = E_{\text{Co}_3\text{O}_4/\text{kaolinite}} - (E_{\text{kaolinite}} + E_{\text{Co}_3\text{O}_4})$, where $E_{\text{Co}_3\text{O}_4/\text{kaolinite}}$, $E_{\text{kaolinite}}$ and $E_{\text{Co}_3\text{O}_4}$ is the total energies of the relaxed Co_3O_4 /Kaol interface, kaolinite surface and Co_3O_4 cluster, respectively. Highly negative adsorption energy indicates it is energetically favorable for kaolinite to load hydrated metal oxide clusters. It is well-known that the deprotonation ability of hydrated oxide surface increases with the increase of metal ions sorption³⁰. Similar to previous work³¹, we have defined the dehydration formation energy as $E_{\text{f}} = 1/n[E_{\text{Co}_3\text{O}_4/\text{kaolinite}-n\text{H}_2\text{O}} - (E_{\text{Co}_3\text{O}_4/\text{kaolinite}} + nE_{\text{H}_2\text{O}})]$, where $E_{\text{Co}_3\text{O}_4/\text{kaolinite}}$, $E_{\text{H}_2\text{O}}$, and $E_{\text{Co}_3\text{O}_4/\text{kaolinite}-\text{H}_2\text{O}}$ are total energies of Co_3O_4 /kaolinite interface, water molecule and Co_3O_4 /kaolinite interface with n H_2O removed.

The support effect of kaolinite on Co_3O_4 greatly facilitates the surface hydrogen bonding, charge transfer and proton diffusion between neighboring hydroxyls for the Co_3O_4 /kaolinite (Fig. 2a) and $\text{R-Co}_3\text{O}_4$ /kaolinite interfaces (Fig. 2b, c). In consideration of

Fig. 3 Structure characterization of $\text{Co}_3\text{O}_4/\text{Kaol}$ catalyst. **a** TEM images of Co_3O_4 , scale bar: 100 nm. **b** TEM images of 5% R- $\text{Co}_3\text{O}_4/\text{Kaol}$, scale bar: 100 nm. **c** High-resolution TEM images of Co_3O_4 , scale bar: 10 nm. **d** High-resolution TEM images of 5% R- $\text{Co}_3\text{O}_4/\text{Kaol}$, scale bar: 5 nm. The amorphous surface layer of one Co_3O_4 nanoparticle is indicated in dashed lines. **e** Raman spectra of the Co_3O_4 , Co_3O_4 (300 °C), and R- Co_3O_4 . **f** Raman spectra of the kaolinite, 5%- $\text{Co}_3\text{O}_4/\text{Kaol}$ and 5% R- $\text{Co}_3\text{O}_4/\text{Kaol}$. **g** The estimated percentage of surface atoms in sphere Co_3O_4 nanoparticles with size from 4 to 10 nm. **h** The outmost surface layer of Co_3O_4 nanoparticles is highlighted in yellow for $\text{Co}_3\text{O}_4/\text{Kaol}$ interface. **i** The bond length distribution of Co_3O_4 , $\text{Co}_3\text{O}_4/\text{Kaol}$, and reduced $\text{Co}_3\text{O}_4/\text{Kaol}$. The major differences are highlighted in gray area. The shortening of O-H bond and elongation of Co-H₂O bond are noticeable

the charge compensation, it is observed that hydrogen atoms favor the deprotonated OH sites on Co-O-Co corner structure and tend to diffuse on Co_3O_4 clusters (Supplementary Movie 1). Similarly, the adsorption of Co_3O_4 clusters on kaolinite surface are much more complicated due to the large number of reactive surface hydroxyl groups. The dehydration energy of kaolinite supported Co_3O_4 nanoparticle was found around 1.3–2.2 eV, which is slightly higher than that of Co_3O_4 nanoparticle (0.7–1.6 eV, Supplementary Figure 2) or Co_3O_4 surface³². The dynamics study demonstrates that less number of H_2O molecules break their bond with Co atoms on supported Co_3O_4 nanoparticle compared to unsupported Co_3O_4 nanoparticle (Supplementary Movie 2). Most significantly, the formation energy of V_{O} for kaolinite supported Co_3O_4 clusters (around -0.6 to 2.4 eV) is much lower than that of unsupported Co_3O_4 clusters (2.5–3.6 eV, Supplementary Figure 3), or bulk Co_3O_4 (3.3 eV)³³. And, the negative formation energy indicates that the reduction process

can occur spontaneously even without additional reduction additives.

The oxygen vacancies introduce defect states in the band gap which are easily excited, create more catalytic and electrochemically active sites, and enhance catalytic reactions or the electrocatalytic activity for oxygen reduction reaction (OER) as reported previously. To illustrate the role of oxygen vacancies in modifying the electronic structure of $\text{Co}_3\text{O}_4/\text{kaolinite}$, the total densities of states and the projected densities of states of both the unsupported Co_3O_4 (Fig. 2d) and the kaolinite supported Co_3O_4 are compared (Fig. 2e). The calculated bandgap of hydrated Co_3O_4 clusters (1.4–1.8 eV) and hydrated $\text{Co}_3\text{O}_4/\text{kaolinite}$ interface (1.4–1.8 eV), which are close to each other are slightly lower than that of bulk Co_3O_4 (1.8 eV)³⁴. Notably, the bandgap of R- $\text{Co}_3\text{O}_4/\text{kaolinite}$ (Fig. 2f) is much lowered (0.52–1.0 eV) due to the formation of oxygen vacancies under strong interface interaction between dangling bonds on dehydrated MO surface

Fig. 4 The support effect of kaolinite on dehydration and reduction properties of Co_3O_4 . **a** TGA curves of Co_3O_4 , Co_3O_4 calcined at 300 $^{\circ}\text{C}$, kaolinite, kaolinite calcined at 300 $^{\circ}\text{C}$, and 5% R- Co_3O_4 /Kaol composites. **b** FT-IR spectra of 5% R- Co_3O_4 /Kaol calcined at different temperatures. **c** XPS Co 2p spectra of 5%- Co_3O_4 /Kaol, 5% R- Co_3O_4 /Kaol and 5%- Co_3O_4 R/Kaol. **d** H_2 -TPR profile of 5% R- Co_3O_4 /Kaol and 5% R- Co_3O_4 /Kaol calcined at different temperatures (300–700 $^{\circ}\text{C}$).

and hydroxyl groups on kaolinite. Besides, the band level of defect states in kaolinite supported Co_3O_4 is more hybridized and diffusive than that in unsupported Co_3O_4 .

The characterization of oxygen vacancies. The X-ray powder diffraction (XRD) patterns for the samples can be readily indexed to kaolinite, while a weak Co_3O_4 diffraction peak at 36.8° was observed on 5% R- Co_3O_4 /Kaol and 10% R- Co_3O_4 /Kaol (Supplementary Figure 4a). The scanning electron microscopy (SEM) image reveals that kaolinite possesses a lamellar structure with a hexagonal appearance and a rough surface (Supplementary Figure 4b). Moreover, the anchoring of Co_3O_4 nanocrystals on 2D kaolinite was confirmed by transmission electron microscopy (TEM) (Fig. 3a, b). The small Co_3O_4 (4–8 nm) originated from the cobalt cations coordinated with NH_3 was anchored on kaolinite surface and further reduction by NaBH_4 solution while the particle remain the same size (Fig. 3c, d, Supplementary Figure 5a–d)³⁵. Furthermore, the supported Co_3O_4 nanoparticles with amorphous surface layer (dashed line) show an interplanar spacing of 0.286 nm, which matches well with the (200) plane of face-centered-cubic phase of spinel Co_3O_4 (Fig. 3d)³⁶. The gray area near grain boundary indicated strong interface bonding between Co_3O_4 and kaolinite, which is further confirmed by Raman spectroscopy (Fig. 3e, f). The Raman spectra of Co_3O_4 , Co_3O_4 calcined at 300 $^{\circ}\text{C}$ and Co_3O_4 reduced with NaBH_4 (R-

Co_3O_4) in Fig. 3e display characteristic peaks at 189 (F_{12g}^1), 468 (E_g), 512 (F_{22g}^2), 607 (F_{22g}^3), and 673 (A_{1g}) cm^{-1} , in consistent with the standard Raman active modes of the Co_3O_4 cubic phase^{37,38}. The blue shift of the Raman band around 650 cm^{-1} for R- Co_3O_4 sample could be attributed to the phonon confinement and distortion around oxygen vacancies³⁹. Obvious differences were found for the Raman bands of 5% R- Co_3O_4 /Kaol and 5%- Co_3O_4 /Kaol, compared to Co_3O_4 or kaolinite (Fig. 3f), indicating strong interface interaction between Co_3O_4 and kaolinite. In order to clarify the nature of this phenomenon, the structures are simulated at atomic level. As can be estimated from the atomic structure of Co_3O_4 clusters (Fig. 3g), there is a huge decrease (from 40 to 15%) of the surface atoms in Co_3O_4 with the increase of Co_3O_4 particle size (from 4 to 10 nm). About one-third of the Co atoms are located in the surface layer of a Co_3O_4 cluster with particle size of 5 nm (Fig. 3h). Based on DFT calculations, for the bond length distribution of Co_3O_4 , Co_3O_4 /Kaol, and R- Co_3O_4 /Kaol (Fig. 3i), the major difference lies on the shortened Co–O bonds (gray area) at interface structures due to the strong adsorption and the elongated Co–O bonds at the corner structure of Co_3O_4 cluster due to the formation of oxygen vacancies after reduction process.

Thermogravimetric analysis (TGA) was used to evaluate composition and structural stability (Fig. 4a). For kaolinite, the small mass loss below 110 $^{\circ}\text{C}$ corresponds to the removal of

Fig. 5 Catalytic performance evaluation of Co₃O₄/Kaol catalyst. **a** Effect of different catalysts on Orange II removal. **b** Recycle test of the catalyst. The catalyst is recycled from the reaction system by simple washing and drying. The decrease of the catalytic efficiency is mainly caused by the mass loss of catalyst during this simple recycle process. Reaction conditions: [Orange II] = 50 mg L⁻¹, [PMS] = 0.5 g L⁻¹, [Catalyst] = 0.1 g L⁻¹. **c** Effects of 5% R-Co₃O₄/Kaol catalysts with different calcination temperatures on Orange II removal. **d** Cyclic voltammetric (CV) curves of the 5%-Co₃O₄/Kaol and the 5% R-Co₃O₄/Kaol on glassy carbon electrodes in 1 M KOH. **e** Linear sweep voltammetry (LSV) curves of the 5%-Co₃O₄/Kaol and the 5% R-Co₃O₄/Kaol. **f** Tafel plots of 5% Co₃O₄/Kaol and the 5% R-Co₃O₄/Kaol

adsorbed water, and the mass loss in the range of 430–600 °C represents the dehydroxylation of the structural Al–OH–Al groups when kaolinite transforms into metakaolinite. After precalcination at 300 °C, the adsorbed water disappears while the bridging Al–OH hydroxyl groups are still retained⁴⁰. The fastest mass loss process between 480 and 520 °C is attributed to the dehydroxylation of kaolinite. The above results confirm that the existence of abundant hydroxyl groups (about 11%) located on the surface of kaolinite. In addition, the dramatic weight loss of Co₃O₄ in the range of 250–350 °C suggests noticeable amount of surface hydroxyl (including chemically bonded water) groups removed during the dehydration process, in contrast to precalcined Co₃O₄ (300 °C) for which the corresponding weight loss is negligible. Notably, compared to pure Co₃O₄ or kaolinite, the weight loss of 5% R-Co₃O₄/Kaol slows down in the range of 300–480 °C due to the retarded dehydroxylation process at Co₃O₄/Kaol interface as demonstrated by DFT calculations (Fig. 1, the calculated dehydration energy of supported Co₃O₄ is lower than unsupported Co₃O₄).

Moreover, Fourier transform infrared spectroscopy (FT-IR) was employed to analyze surface groups under different calcination conditions. While for kaolinite (Supplementary Figure 6) or Co₃O₄ nanoparticles (Fig. 4b), the broad bands of adsorbed water (near 3400 and 1600 cm⁻¹) disappeared above 300 °C, for 5% R-Co₃O₄/Kaol, these adsorbed water are partially retained (Supplementary Figure 7). The stability of these bonded water at interface structure along with the intrinsic hydroxyl groups on kaolinite surface, as a key factor to modulate V_O of metal oxide, are tested in water (Supplementary Figure 8).

In order to clarify the formation of oxygen vacancies at the interfacial structure between MO and clay material, X-ray photoelectron spectroscopy (XPS) analysis were performed. High-

resolution Co 2p spectra verify the ratio of Co²⁺/Co³⁺ in three samples follows the order: 5% R-Co₃O₄/Kaol > 5%-Co₃O₄R/Kaol ≈ 5%-Co₃O₄/Kaol (Fig. 4c), which reflects that more vacancies were generated in 5% R-Co₃O₄/Kaol⁴¹. The peaks at ~780.1 eV and ~781.6 eV are indexed to Co³⁺ (Co 2p_{3/2}) and Co²⁺ (Co 2p_{3/2}), respectively⁴². The slight shift of Co 2p peak of 5% R-Co₃O₄/Kaol to higher binding energy could be attributed to the strong interface bonding between Co₃O₄ and kaolinite. In addition, the emergence of satellite peak (sat.) implies the generation of more Co²⁺ species⁴³. As the concentration of reductants increases from 0.05 to 0.2 M, the Co²⁺ species increase slowly (Supplementary Figure 9a). Notably, very low concentration of reducing agent is needed for the kaolinite supported Co₃O₄ (5% R-Co₃O₄/Kaol 0.05 M) to produce similar amount of Co²⁺ for Co₃O₄ (0.5 M) (Supplementary Figure 9b), which demonstrated the easy formation of oxygen vacancies at Co₃O₄/Kaol interface as predicted by DFT calculations. Although metal cation vacancies would have a significant effect on the catalytic activity⁴⁴, cation vacancies are not detected during the reduction under NaBH₄, which excluded the simultaneous formation of cation vacancies. The XPS survey spectra of the different samples are given in Supplementary Figure 10. We also measured the change of binding energy of Co 2p and O 1s in R-Co₃O₄/Kaol under different calcination temperature (Supplementary Figure 11). The increase of Co²⁺ in R-Co₃O₄/Kaol under higher calcination temperature suggests the further modulation of oxygen vacancy by dehydroxylation process. No obvious shift of the binding energy of O1s, C1s, Al 2p, and Si 2p are found (Supplementary Figures 12 and 13)⁴⁵. Besides, the existence of Vo in the R-Co₃O₄/Kaol was also measured by electron paramagnetic resonance (EPR) spectroscopy⁴⁶. Generally, the intensity means the concentration of Vo. The reduced Co₃O₄/Kaol shows a much stronger EPR signal than pristine Co₃O₄/Kaol,

revealing the generation of abundant oxygen vacancies in R-Co₃O₄/Kaol⁴⁷ (Supplementary Figure 14).

To obtain a deeper understanding of how hydroxyl group interacts with oxygen vacancies, the reduction properties of samples were tested using H₂-temperature programmed reduction (H₂-TPR) (Fig. 4d). For 5% R-Co₃O₄/Kaol (300 °C), the reduction peaks in the range of 280–410 °C could be attributed to the Co³⁺ → Co²⁺ reduction of Co₃O₄ nanoparticles under the retardant effect of hydroxyl group, which are much higher than that of unsupported Co₃O₄ nanoparticles with size of about 20 nm⁴⁸. For 5% R-Co₃O₄/Kaol (500 °C), three peaks are shifted to the lower region due to the weakening of the retardant effect since hydroxyl groups are partially removed. Finally, for 5% R-Co₃O₄/Kaol (700 °C), the separated peaks are merged into one reduction peak (358 °C) due to the complete removal of the hydroxyl groups on kaolinite. The peak at 714 °C can be assigned to the reduction of cobalt silicate generated at Co₃O₄/Kaol interface⁴⁹. In a word, the above results further confirm that kaolinite can modulate the reducibility of Co₃O₄ by controlling the amount of hydroxyl groups on kaolinite to modulate vacancy defects.

Catalytic performance evaluation. Orange II (C₁₆H₁₁N₂NaO₄S) dyes belong to a class of organic compounds known as an anionic azo-dyes⁵⁰, which are widely used in industries⁵¹. In addition, they are stable with respect to biological degradation and sometimes may produce more hazardous intermediates in wastewater treatment processes⁵². Advanced oxidation processes are effective remediation to degrade orange II azo-dye from an aqueous solution⁵³. As shown in the degradation test of Orange II, 5% R-Co₃O₄/Kaol exhibited higher catalytic activity compared to 5%-Co₃O₄/Kaol and 5%-Co₃O₄R/Kaol (Fig. 5a), and good regeneration stability (Fig. 5b). The reduced Co₃O₄/Kaol samples showed enhanced catalytic activity compared to pristine samples (Supplementary Figure 15), which can be attributed to the facilitated reactive oxygen production by oxygen vacancies when react with peroxymonosulfate (PMS). Note that the samples prepared at higher temperature which have less hydroxyl groups at Co₃O₄/Kaol interface showed decreased catalytic efficiency, implying the importance of hydroxyl groups on modulating catalytic activities (Fig. 5c)⁵⁴. Besides, the negligible degradation of Orange II over PMS or 5% R-Co₃O₄/Kaol indicated the crucial role of their synergistic effect on the degradation reactions (Supplementary Figure 16). Based on above results, it could be speculated that a great enhancement in the catalytic activity could be possibly attributed to the following reasons: the coupled interface of Co₃O₄/Kaol, the generation of oxygen vacancies and the frequent cycle reaction between divalent cobalt ion and trivalent cobalt ion.

Benefiting from its PMS activation behavior, the effects of different conditions such as NaBH₄ concentrations, catalyst dosages, PMS dosage, reaction temperatures, and solution pH (Supplementary Figures 17 and 18) as well as coexisting anions (Supplementary Figure 19) on the catalytic efficiency were also investigated. To confirm the reactive oxygen species, the radical scavenger tests were conducted using tert-butyl alcohol (TBA) and methanol (Supplementary Figure 20). Methanol exhibited an obvious inhibitory effect on the degradation of Orange II, due to the scavenging of sulfate radical by methanol (MeOH)^{55,56}. The possible mechanism of the highly efficient catalyst could be summarized (Supplementary Note 1). These results confirm the significant practical application of as-prepared catalyst in the treatment of wastewater with various anions and also provide a reasonable evidence to support the role of oxygen vacancies.

To further verify the role of kaolinite for modulate oxygen vacancy of MO, the samples were also investigated as electrocatalyst for oxygen evolution reactions. According to the CV curves of pristine 5%-Co₃O₄/Kaol and reduced 5% R-Co₃O₄/Kaol samples (Fig. 5d), the V_O-rich 5% R-Co₃O₄/Kaol shows a distinct current density, which suggests massive electrochemically active site existed on the surface of catalyst⁵⁷. Moreover, the V_O-rich catalyst possesses much higher OER catalytic activity than pristine catalyst (Fig. 5e). At a potential of 1.65 V (vs. RHE), the reduced Co₃O₄/Kaol exhibit a current density of 1.05 mA cm⁻², i.e., >4 times higher than the pristine one (0.26 mA cm⁻²)⁵⁸. Similarly, V_O-rich Co₃O₄/Kaol exhibits a smaller Tafel slope than pristine sample (Fig. 5f)⁵⁹, which means a faster increase of the OER rate with the increasing potential and could benefit the OER performance of Co₃O₄.

Moreover, electrochemical impedance spectroscopy (EIS) analyses were employed to evaluate the charge transfer capability on the surface of catalysts in PMS and Na₂SO₄ solutions (Supplementary Figure 21a). The 5% R-Co₃O₄/Kaol has relatively lower charge transfer resistance than the pristine 5%-Co₃O₄/Kaol sample, because oxygen vacancies play a pivotal role in the charge transfer process. In addition, photoluminescence (PL) measurements were employed to analyze the separation and recombination of charge carriers in Co₃O₄/Kaol (Supplementary Figure 21b). Compared to the pristine sample, the emission band of 5% R-Co₃O₄/Kaol at ~420 nm obviously decreases, which may promote the separation of charge and contribute to the enhanced redox reaction⁶⁰. The generated oxygen vacancies could not only enhance their catalytic activity, delocalize electrons on/near the nanoparticles surface, but also dramatically increase the electronic conductivity.

Discussion

In conclusion, DFT calculations have revealed that the hydroxyl groups on the clay surface would promote the formation of V_O on the supported oxides when they are dehydrated upon calcination process. The enhanced reduction ability of Co₃O₄/Kaol during the adsorption, dehydration and reduction process is clarified as interface bonding, surface distortion and proton transfer mechanisms at atomic level. The concentration of oxygen vacancies in Co₃O₄ nanocrystals can be modulated by the hydroxyl groups on clay support, the interface of which can act as active centers for catalytic oxidation reaction. In this work, it is found that the synergistic effect of clay support enhanced the concentration of V_O on Co₃O₄ surface and modified the redox activity of Co (due to the lowered formation energy under charge compensation of protons from hydroxyl groups of kaolinite), and meanwhile lead to the higher dispersion of nano-Co₃O₄ and stronger adsorption of organic pollutant on kaolinite (due to the hydrophilic surface of kaolinite), which finally lead to the enhanced catalytic activity at Co₃O₄/clay interface. It should be noted that this finding also applies to other reducible metal oxide. This work not only provides insights into the fundamental understanding of the support effects such as strong adsorption and enhanced reducibility of clay on metal oxide catalysts, but also experimentally demonstrates the modulation of oxygen vacancies, i.e., the redox activity of MO in oxide/clay nanocomposites using earth-abundant clay minerals as support material for enhanced catalytic performance.

Methods

Materials. Natural kaolinite was obtained from China Kaolinite Clay Co., Ltd. (Suzhou, China), and its chemical compositions are as follows: SiO₂ 53.27%, Al₂O₃ 42.46%, SO₃ 2.19%, K₂O 0.54%, Fe₂O₃ 0.48%, TiO₂ 0.33%, P₂O₅ 0.26%, MgO 0.16%, CaO 0.09%, and CuO 0.01%. Cobalt acetate tetrahydrate Co(CH₃COO)₂·4H₂O, ethanol (EtOH), orange II (C₁₆H₁₁N₂NaO₄S), ammonium hydroxide (NH₃·H₂O),

methanol (MeOH), sodium borohydride (NaBH_4), TBA, and PMS ($\text{KHSO}_5 \cdot 0.5\text{KH}_2\text{SO}_4 \cdot 0.5\text{K}_2\text{SO}_4$) were purchased from Sinopharm Chemical Reagent Co. Ltd. Deionized water was used in all experiments. All chemicals are of analytical grade reagents and were used as received without further purification.

Synthesis of Co_3O_4 nanocrystals. In a typical experiment, 3 mL of 0.2 M $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ aqueous solution was added to 48 mL of ethanol to form a clear solution, followed by the addition of 2 mL of $\text{NH}_3 \cdot \text{H}_2\text{O}$. The above solution was stirred for 8 h at 80 °C. After that, the resulting solution was subsequently transferred to an autoclave for hydrothermal reaction at 150 °C for 3 h. The product was washed with water and ethanol for several times.

Synthesis of Co_3O_4 /Kaol. The Co_3O_4 /kaolinite (Co_3O_4 /kaol) was prepared by mixing two different solutions: solution A contained a certain amount of Co_3O_4 nanocrystals in 10 mL ethanol and was treated with ultrasound for 30 min. Solution B included 0.2 g kaolinite in 20 mL ethanol and was ultrasonicated for around 30 min. The mass ratios of Co_3O_4 to kaolinite were kept at 0.5%, 1%, 2%, 5%, and 10%, respectively. Solution B was continuously stirred for 10 min to disperse completely, to which the solution A was added dropwise. After reaction for 1 h, the products were dried in an oven at 80 °C for 12 h, then, calcined in a muffle furnace at 300 °C for 2 h in air with a heating rate of 5 °C min^{-1} and allowed to cool naturally to room temperature. The final products were labeled as 0.5%- Co_3O_4 /Kaol, 1%- Co_3O_4 /Kaol, 2%- Co_3O_4 /Kaol, 5%- Co_3O_4 /Kaol, and 10%- Co_3O_4 /Kaol.

Synthesis of reduced Co_3O_4 /Kaol. The reduced samples were prepared by stirring pristine Co_3O_4 /Kaol nanocomposites in 0.05 M NaBH_4 solution for 30 min, then the suspension was washed with water and ethanol, solid samples were dried at 60 °C for 10 h. The final products were labeled as 0.5% R- Co_3O_4 /Kaol, 1% R- Co_3O_4 /Kaol, 2% R- Co_3O_4 /Kaol, 5% R- Co_3O_4 /Kaol, and 10% R- Co_3O_4 /Kaol, respectively.

Synthesis of reduced Co_3O_4 and kaolinite nanocomposites. The samples were prepared by stirring Co_3O_4 calcined at 300 °C for 2 h in 0.05 M NaBH_4 solution for 30 min, then the suspension was washed with water and ethanol, solid samples were dried at 60 °C for 10 h. A certain amount of treated Co_3O_4 nanocrystals were added to 10 mL ethanol and sonicated for 30 min, then, 0.2 g kaolinite was dispersed in 20 mL ethanol and ultrasonically dispersed for 30 min, respectively. The mixture of the above two different solution was stirred 1 h, and the suspension was dried at 60 °C for 10 h. The final product was labeled as 5%- Co_3O_4 R/Kaol, respectively.

Synthesis of R- Co_3O_4 /Kaol (500 and 700 °C). The synthesis of 5% R- Co_3O_4 /Kaol (500 and 700 °C) was similar to the one of reduced Co_3O_4 /Kaol, and the difference was that 5% R- Co_3O_4 /Kaol (500 and 700 °C) was prepared at different calcination temperatures (500 and 700 °C), otherwise reduced Co_3O_4 /Kaol was prepared at 300 °C calcination.

Materials characterization. XRD patterns (2 θ , 5–70°) were recorded by using a Bruker-AXS D8 Advance diffractometer with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$). SEM was performed on a Tescan Mira3 LMU instrument. Transmission electron microscope (TEM) and high-resolution TEM were obtained on Titan G2 60–300 microscope operating at 300 kV and FEI Tecnai G2 f20 microscope operating at 200 kV, respectively. (FT-IR) was measured using a Bruker Tensor 27 spectrophotometer. (TGA) was carried out on a thermal analyzer (Netzsch sta 449F3). H_2 -temperature programmed reduction (H_2 -TPR) was conducted on a Finesorb 3010H physico-chemical adsorption apparatus. Raman test was run on a LabRAM HR (wavelength = 532 nm). (XPS) measurements were obtained using an ESCA-LAB 250 Xi spectrometer. EPR tests were carried out in Bruker A300. Electrochemical impedance spectroscopy (EIS) measurements were performed in a conventional three-electrode cell using a CHI760D electrochemical workstation. The PL was measured on a Hitachi F-7000 fluorescence spectrophotometer.

Catalytic degradation procedure. For the organic pollutant degradation process, Orange II dye was selected as a model pollutant. In a typical test, 3 mg of catalyst was first added to 30 mL of Orange II solution with an initial concentration of 50 mg L^{-1} at room temperature without pH adjustment. Then the suspension was stirred for 15 min to establish the adsorption–desorption equilibrium. Afterwards, the catalytic reaction was triggered by adding a small quantity of PMS solution. At various time intervals, 1 mL of mixture solution was extracted from the reactor and quenched with 1 mL of methanol. The concentration of Orange II ($\lambda = 486 \text{ nm}$) was determined using a UV–vis spectrometer.

OER measurements. The oxygen reduction reaction (OER) properties were carried out using an electrochemical workstation (Metrohm, Switzerland) with a three-electrode system in 1 M aqueous KOH solution. The synthesized electrode was applied to the working electrode. A drop casting method was used to prepare catalysts on the glassy carbon (GC). Typically, a sample slurry was prepared by

mixing 1 mL of ethanol, 5 mg of sample and 25 μL of Nafion (5 wt%, Aldrich), followed by sonicated for 30 min to obtain the catalyst ink. Then a suitable amount of the slurry was transferred onto the GC electrode working area with a constant catalyst loading of 0.07 mg cm^{-2} . Pt sheet work as the counter electrode, saturated calomel as the reference electrode. The cyclic voltammetric (CV) measurements were conducted performed with the scan rate of 50 mV s^{-1} and linear sweep voltammetry curves were performed with the scan rate of 20 mV s^{-1} . The Tafel slope can be obtained by using Tafel equation. According to the beginning of the linear region in Tafel plots, the onset potentials can be determined.

Computational details. All calculations were performed with the program CASTEP (Cambridge Sequential Total Energy Package) code, with the exchange–correlation potential by Perdew, Burke and Ernzerhof (PBE)⁶¹ and dispersion corrections by Grimme (PBE-D2)⁶². The ultrasoft pseudo-potential plane-wave formalism with energy cutoff of 500 eV and density-mixing scheme was used^{63,64}. For electronic structure calculations, the GGA + U method was used with the U_{eff} ($=U-J$) parameter set to 3 eV for the 3d electrons of Co atom. The Monkhorst–Pack⁶⁵ grid with $2 \times 2 \times 1$ k points mesh was used for electronic structure calculations, while Gamma point was used for geometrical calculations. During geometry optimizations, the convergence threshold for self-consistent field tolerance was set to $1.0 \times 10^{-6} \text{ eV atom}^{-1}$, all forces on the atoms were converged to less than 0.03 $\text{eV \AA}^{-1}$, and the maximum ionic displacement was within 0.001 $\text{\AA}$. The original structure of kaolinite $\text{Al}_2(\text{Si}_4\text{Al}_2\text{O}_{10}(\text{OH})_2)$ with $2\sqrt{2} \times \sqrt{2} \times 1$ supercell (8 kaolinite units) was taken from previous work. Under Broyden–Fletcher–Goldfarb–Shanno minimization algorithm, the cell parameters and atomic coordination of all structures were fully relaxed. After the relaxation of bulk kaolinite, the slab structure of kaolinite surface are constructed by adding 15 $\text{\AA}$ vacuum in (001) direction, then the c axial is kept fixed during the relaxation. Co_3O_4 is adsorbed only on top side of kaolinite slab, and we verified that the dipole correction of kaolinite surface and the image interactions between Co_3O_4 clusters are negligible. H_2O molecules and Co_3O_4 cluster structures are confined in 20 $\text{\AA}$ box. The bottom Si–O layer of kaolinite surface is fixed during the adsorption of Co_3O_4 cluster. For the Co_3O_4 cluster, two symmetric structures with anti-ferromagnetic ground state are considered, a small cluster ($\text{Co}_{13}\text{O}_{38}\text{H}_{43}$) and a large cluster ($\text{Co}_{24}\text{O}_{64}\text{H}_{64}$). Since the later requires a larger slab structure of kaolinite ($\text{Al}_{32}\text{Si}_{32}\text{O}_{80}(\text{OH})_{64}$ with $4 \times 2 \times 1$ supercell) to load Co_3O_4 cluster which is computational demanding, in this work we adopted $\text{Co}_{13}\text{O}_{38}\text{H}_{43}$ cluster for the Co_3O_4 /Kaol interface structure. During the dehydration process (simulate the calcination process), the $-\text{H}_2\text{O}$ groups are removed gradually from Co_3O_4 cluster. For the dehydrated Co_3O_4 ($\text{D-Co}_3\text{O}_4$, $\text{Co}_{13}\text{O}_{31}\text{H}_{29}$) cluster, about one-third of (the longest) surface $-\text{H}_2\text{O}$ groups are removed from the Co_3O_4 cluster. Then, we can obtain the reduced Co_3O_4 (R- Co_3O_4 , $\text{Co}_{13}\text{O}_{30}\text{H}_{29}$) cluster by removed one O atom from the dehydrated Co_3O_4 cluster. Ab initio molecular dynamics simulations were carried out at 273 or 573 K by a Nose thermostat set using a statistical ensemble with fixed particle number, volume and temperature. The time step was set to 1 fs, and the systems were equilibrated for more than 1 ps.

Data availability

The authors declare that the main data supporting the findings of this study are available within the paper and its Supplementary Information file. Other relevant data are available from the corresponding author upon reasonable request.

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Author contributions

Q.Z. and L.F. contributed equally to this work. H.Y. conceived the project. Q.Z. and L.F. wrote initial drafts of the work. Y.X. offered the help in revising the drafts. H.Y. wrote the final paper. L.F. performed the density functional theory calculations and related analysis. Q.Z. designed the experiments, synthesized, and characterized the materials. Q.Z., H.Y., Y.H., D.J., and J.O. analyzed the data. All authors discussed the results and commented on the manuscript.

Additional information

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