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An efficiently tuned d-orbital occupation of IrO₂ by doping with Cu for enhancing the oxygen evolution reaction activity†

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The oxygen evolution reaction (OER) has been regarded as a key half reaction for energy conversion technologies and requires high energy to create O=O bonds. Transition metal oxides (TMOs) seem to be a promising and appealing solution to the challenge because of the diversity of their d-orbital states. We chose IrO₂ as a model because it is universally accepted as a current state-of-the-art OER catalyst. In this study, copper-doped IrO₂, particularly Cu_{0.3}Ir_{0.7}O_δ, is shown to significantly improve the OER activity in acidic, neutral and basic solutions compared to un-doped IrO₂. The substituted amount of Cu in IrO₂ has a limit described by the Cu_{0.3}Ir_{0.7}O_δ composition. We determined that the performance of Cu_{0.3}Ir_{0.7}O_δ is due primarily to an increase in the Jahn–Teller effect in the CuO₆ octahedra, and partially to oxygen defects in the lattice induced by the IrO₆ octahedral geometric structure distortions, which enhance the lift degeneracy of the t_{2g} and e_g orbitals, making the d_{z²} orbital partially occupied. This phenomenon efficiently reduces the difference between ΔG₂ and ΔG₃ in the free energy from the density functional theoretical (DFT) calculations and can yield a lower theoretical overpotential comparable to that of IrO₂. The proposed method of doping with foreign elements to tune the electron occupation between the t_{2g} and e_g orbital states of Ir creates an opportunity for designing effective OER catalysts using the TMO groups.

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Introduction

The oxygen evolution reaction (OER) at the anode is the key half reaction for splitting water into H₂ fuel and reducing the CO₂ concentration in fuels (*e.g.*, CO, CH₄) and metal–air batteries.^{1–4} However, the OER is a complex process associated with 4e/4H⁺ loss and O=O bond formation, which requires a high overpotential relative to the standard reaction potential ($E = 1.229$ V, pH = 0) to achieve the desired current density.^{1,5,6} The critical step to address the challenge is to find efficient catalysts. One of the most promising catalysts is a transition metal oxide (TMO); this group has nearly infinitely variable properties of its d-orbital states (d⁰ ~ d¹⁰),^{7,8} particularly t_{2g} and e_g, which can be

systematically modified to optimize the catalytic activity at the surface.^{9–11} The OER catalytic activity of TMOs is governed completely by its d-orbital electron structure¹² because the bond making or breaking in the OER processes are based on the O-2p of intermediates bonding with the M-nd of surface sites. Many approaches are being engineered to enhance the OER catalytic activity by doping foreign elements into the host structure or modifying the substitute to increase the number of catalytically active sites.^{13–18} Numerous studies show that introducing F,¹⁹ Ru,^{20,21} Ta²² and Zn²³ into IrO₂ can obtain an improvement in the OER activity. However, there are still important aspects regarding how the doped foreign metals tune the d orbital electronic structure of the host element and further affect its OER activity.

Here, we show that copper (Cu)-doped IrO₂, particularly in the Cu_{0.3}Ir_{0.7}O_δ composition, exhibits a high OER activity in acidic, neutral and basic solutions (pH ~ 1, 7 and 13, respectively). We chose IrO₂ as a model because it has been universally accepted as a current state-of-the-art OER catalyst and maintains a stable structure in water oxidation over a broad pH range.^{24–27} The copper is taken as the dopant due to its special electronic structure (3d¹⁰4s¹), and Cu²⁺ is widely applied in superconductors.^{28–30} In this study, the Cu that is introduced into the IrO₂ lattice changes the IrO₂ lattice parameters and further affects the d-orbital distributions of the Ir-5d electrons; these mechanisms are discussed in detail. We also attribute the

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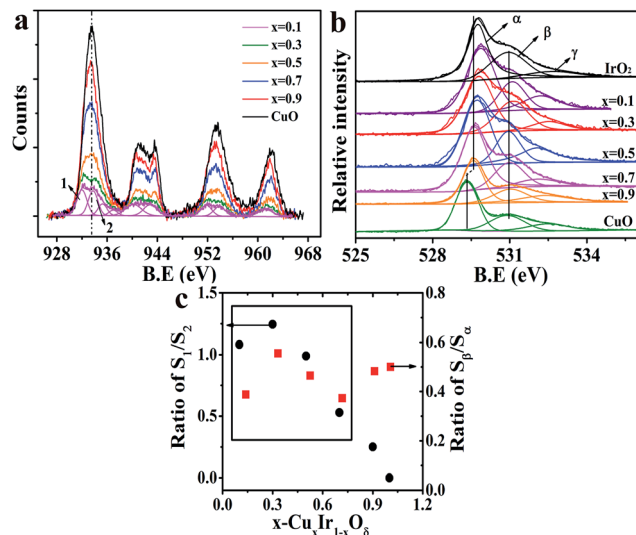


Fig. 4 (a) XPS spectra of Cu-2p in the $\text{Cu}_x\text{Ir}_{1-x}\text{O}_6$ compositions with $x = 0.1$ de-convoluted; other compositions' de-convoluted spectra are shown in the ESI. (b) XPS spectra of O-1s in the $\text{Cu}_x\text{Ir}_{1-x}\text{O}_6$ compositions. (c) Pattern of the ratio of S_1/S_2 and S_β/S_α versus the doped amount x .

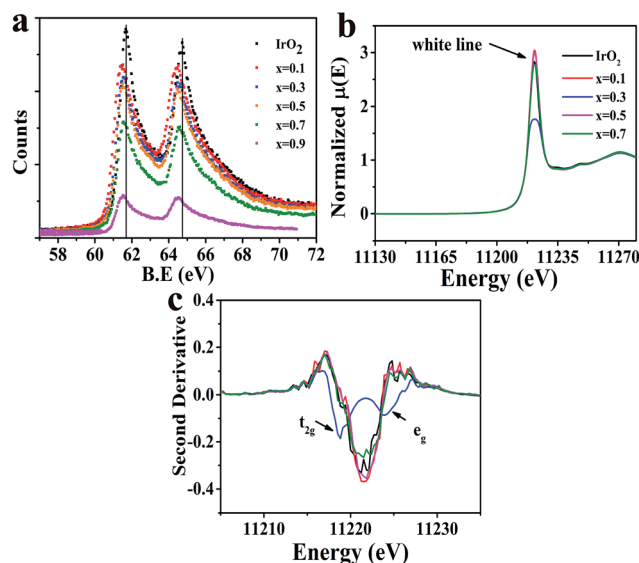


Fig. 5 (a) XPS spectra of Ir-4f in $\text{Cu}_x\text{Ir}_{1-x}\text{O}_6$ compositions. The solid vertical lines correspond to the Ir-4f_{7/2} and 4f_{5/2} peak positions of IrO_2 . (b) Normalized Ir-L_{III} edge XANES spectra for $\text{Cu}_x\text{Ir}_{1-x}\text{O}_6$ compositions. (c) Second derivatives of Ir-L_{III} edge XANES spectra for $\text{Cu}_x\text{Ir}_{1-x}\text{O}_6$ compositions.

systems present. It was also confirmed by performing EDX mapping (Fig. S4†) that Cu was homogeneously doped into the IrO_2 lattice with a low Cu composition (for $x = 0.1$ and $x = 0.3$).

These results were confirmed by the Cu-K edge X-ray absorption near-edge structure (XANES), as shown in Fig. 3a. The Cu-K edge of the CuO separated into two regions in planar symmetry, which were a $1s \rightarrow 4p_z$ transition, corresponding to the low energy peak (*i.e.*, the shakedown peak), and $1s \rightarrow 4p_{x,y}$

transitions, corresponding to the primary edge.³⁶ The local symmetry of Cu, however, had changed to an octahedral symmetry as Cu substituted into Ir sites, and the shakedown peak disappeared due to the isotropic 4p orbital.^{36,37} Therefore, no shakedown peak was observed at $x = 0.1$ and 0.3 in the XANES, which was confirmed by the extended X-ray adsorption fine structure (EXAFS) of the Cu-K edge shown in Fig. S5.† However, the intensity of $x = 0.3$ is shown to be above that of $x = 0.1$, which indicated that the octahedron might be distorted. All of the samples studied showed a weak pre-edge peak, which was assigned to $1s \rightarrow 3d$ due to the quadruple-allowed transition (see Fig. 3a II); this intensity could be achieved by the metal 4p_z orbital mixing into the 3d orbitals; however, this is not possible due to centrosymmetric complexities.^{36–39} A significant feature was also noted: the peak intensity of the doped samples was above that of CuO, indicating the excited distortion of the CuO_6 octahedra at $x = 0.3$ and 0.5.

As shown, the Cu doping produces an elongated IrO_6 octahedron due to the CuO_6 octahedron's strong Jahn-Teller effect,^{40,41} in which the four equatorial oxygen atoms form a plane that compresses, while the apical oxygen out of the plane forms an extended octahedron. The IrO_2 rutile structure exhibits edge sharing along the c axis to form chains, and each chain is linked with four neighboring chains by their shared corners (see Fig. 2b). The Ir-O bonds of the IrO_6 octahedra are not equal⁴² ($4L + 2S$) and include four longer Ir-O bonds in plane along with two short ones that correspond to the apical O. As mentioned above, as a result of the Jahn-Teller effect of CuO_6 , the apical O in the CuO_6 octahedron is out of plane, compressing the equatorial O of the neighboring Ir site, and compressed Cu-O bonds of the plane likely make the neighboring apical Ir-O bonds longer. The XRD data of the compounds shows that the shift values of the (110) plane, which describes the a axial length, were smaller compared to (101) and (211), which are both represented by a and c axial lengths. This results in the axial ratio c/a , a critical parameter for the rutile structure, being decreased compared to that of IrO_2 . The calculated lattice parameters of all samples are listed in Table S3† based on the XRD data. The results of the performed selected area electron diffraction (SAED) are shown in Fig. S2† and show that the d -space of the specified planes decreased after Cu doping. The HRTEM of the samples shown in Fig. S6† also revealed that the d -space of the (200) plane was similar between the Cu-doped samples and IrO_2 . The data extracted from the EXAFS spectra (see Fig. S7†) of the Ir-L_{III} edge also showed that the Ir-O bond lengths are marginally longer than those of IrO_2 in the samples doped with Cu, while the Ir-Ir peak corresponding to the c axis decreased significantly compared to IrO_2 , indicating a reduced c/a ratio, which is consistent with the XRD and SAED data discussed above. All of these data indicate that the IrO_2 doped with Cu had a significant lattice distortion with elongated Ir-O bonds for apical O and compressed Ir-O bonds for equatorial O.

It has been shown that oxygen vacancies (Vo)^{43,44} will be generated due to the substituted Cu occupying the lattice sites of Ir because the dopant (Cu) charge (+2) is different to the host (Ir) charge (+4); the crystal must maintain its electrical



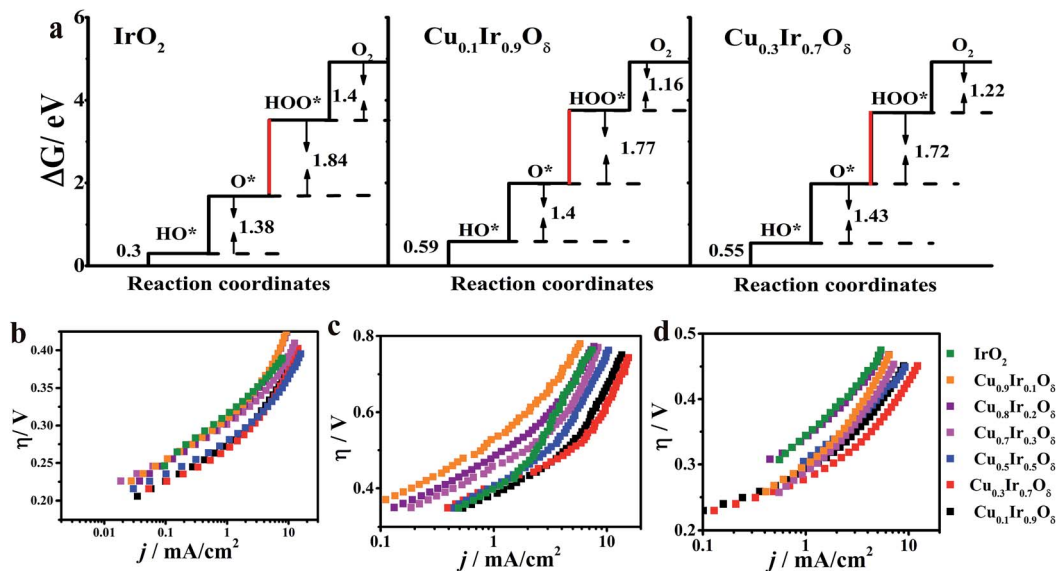


Fig. 7 (a) Standard free energy diagram for the OER in IrO_2 , $\text{Cu}_{0.1}\text{Ir}_{0.9}\text{O}_8$ and $\text{Cu}_{0.3}\text{Ir}_{0.7}\text{O}_8$. (b–d) Tafel plots in acidic, neutral and basic solutions, respectively. The curves are iR-corrected in the acidic ($\sim 18 \Omega$), neutral ($\sim 15 \Omega$) and basic ($\sim 28 \Omega$) solutions, respectively. The catalyst mass loading was $\sim 0.2 \text{ mg cm}^{-2}$ for all electrodes.

occupy the t_{2g} triplet (*i.e.*, d_{xz} , d_{yz} and $d_{x^2-y^2}$) and leave the higher e_g doublet (*i.e.*, d_{xy} and d_z^2) empty under the octahedral crystal field described by the $t_{2g}^5 e_g^0$ configuration.^{45,46} However, as shown in the second derivative spectra (Fig. 5c), only a single feature was observed for IrO_2 due to the IrO_6 octahedron being cross-linked to form a 3D structure; this can be explained by a bond model.^{47,48} In contrast, the doublet feature was found in some iridate perovskite compositions with the IrO_6 octahedron being regarded as a single cluster. Therefore, Fig. 5c confirms that $x = 0.3$ produces a doublet in the white line structure, and other doped compositions yielded results similar to that of IrO_2 . One of surprising features at $x = 0.3$ was that the peak intensity and area of the $2p \rightarrow t_{2g}$ ($5d$) transition were increased above those of the $2p \rightarrow e_g$ ($5d$) transition, which are in contrast to the findings in iridate perovskites;^{47,48} thus, we inferred that the e_g state had been partially occupied.

The Cu doping led to an IrO_2 lattice distortion due to the CuO_6 octahedron's Jahn–Teller effect and also generated oxygen defects, which significantly affected the energy distribution of the d-orbitals of Ir sites. The density of states (DOS) is a good descriptor for the bonding character and occupancy of the orbital states.^{49–52} Fig. 6a and b showed the DOS of IrO_2 and the doped material at $x = 0.1$ and 0.3 using the general gradient approximation (GGA) calculation; details of this analysis are shown in the calculation section of the ESI.† The colored region of Fig. 6a labels α , β , γ , ε and ϕ for Ir–O a_{1g} bonding, σ bonding, π bonding, π antibonding (including the non-bonding part) and σ antibonding, respectively.^{46,53,54} One of the features of DOS is that the σ and π bonding region changed from narrow to relatively broad, and its antibonding states were pulled to a lower energy level as the Cu doping increased, weakening the bonding; this was primarily due to the occupancy of σ states. The partial DOS (PDOS) of Ir is shown in Fig. 6b. The d_{xy} orbital occupied states were located at lower energies (gray solid line),

while the antibonding states moved to higher energies (light blue region) as the Cu doping amount increased, indicating that the d_{xy} orbital was uplifted. In contrast, the d_z^2 antibonding states were shifted to a lower energy level. The d_{xz} and d_{yz} bands were crossed by the Fermi level (E_F), which changed to a narrow shape and was pushed above E_F , indicating that the bands were empty in the π antibonding orbital; this indicated that the electrons may be half-filled in the d_{xz} and d_{yz} orbital. The $d_{x^2-y^2}$ band showed nearly no variation when fully occupied, even when doped with Cu. As discussed above, the Ir-5d electrons showed lifted degeneracy in the octahedron within Cu; this made the d_z^2 orbital energy decrease, while the d_{xy} orbital energy increased. As a result, an electron might hop to the d_z^2 orbital (see Fig. 6c), making the e_g orbital partially filled.

Based on the density functional theory (DFT) and the molecular orbital principles, a strong or weak bond formation from a surface site interacting with the reaction intermediates is strongly correlated with the OER activity. A σ bond to a e_g orbital facilitates bonding with oxygen intermediates compared to a π bond t_{2g} orbital due to the e_g orbital's stronger overlap with O-2p.^{8,52,55} Suntivich *et al.*⁵⁵ proposed that e_g occupation close to unity optimizes the rate-determining step (RDS) and thereby leads to a higher OER activity and is successful in perovskite studies. Vojvodic and Nørskov⁵² showed that the surface-oxygen bond energy correlates with e_g and t_{2g} occupation and has a similar relationship to the interaction between the surface site and O-adsorbate, which becomes weaker with an increasing number of occupied states (*e.g.*, e_g and t_{2g}). The possible OER mechanism on the metal oxides is shown in Fig. S10.† The binding free energies of all the reaction intermediates (HO^* , O^* , HOO^*) involved in Fig. S9† are described in Fig. 7a. For a wide class of metal oxides, a linear relationship was found in the binding free energy between OH^* and O^* equated with $\Delta G_2 + \Delta G_3 = 3.2 \pm 0.2 \text{ eV}$.^{50,56} As a result, the catalysts have been



optimized, evidenced by the reduction in the difference between ΔG_2 and ΔG_3 . It was found that the sum of ΔG_2 and ΔG_3 met this relationship for IrO_2 (3.22 eV), $\text{Ir}_{0.9}\text{Cu}_{0.1}\text{O}_\delta$ (3.17 eV) and $\text{Ir}_{0.7}\text{Cu}_{0.3}\text{O}_\delta$ (3.15 eV). In the case of IrO_2 ($t_{2g}^5e_g^0$), partial e_g filling on the Ir sites may result in the electrons of the O-2p adsorbate being able to easily hop to the unoccupied σ^* orbital to form Ir–OH and Ir–O bonds, which decrease the free energies of the first and second step (OH* and O*). However, the formation of OOH* will occur at the RDS ($\Delta G_3 = 1.84$ eV) due to the rupture of the surface-oxygen bonds in most of the metal-oxide catalysts. For IrO_2 doped with Cu ($x = 0.1$ and 0.3) with e_g partially filled on the Ir site, it should take a higher energy to form Ir–OH and Ir–O bonds ($\Delta G_1 + \Delta G_2 = 1.99$ and 1.98 eV higher 1.68 eV of IrO_2); however, the difference between ΔG_2 and ΔG_3 was found to be decreased ($\Delta G_3 - \Delta G_2 = 0.37$ eV and 0.29 eV comparable to 0.46 eV of IrO_2) and reached a lower theoretical overpotential ($\eta_{\text{the}}(x = 0.3) = 0.39$ eV with $\eta_{\text{the}}(x = 0) = 0.51$ eV). The experimental data of OER for the studied samples are shown in Fig. 7b–d, which show that, except for $\text{Cu}_{0.3}\text{Ir}_{0.7}\text{O}_\delta$, all doped materials exhibited some OER activity; the $\text{Cu}_{0.2}\text{Ir}_{0.8}\text{O}_\delta$ and $\text{Cu}_{0.1}\text{Ir}_{0.9}\text{O}_\delta$ compositions had a higher j compared to IrO_2 in the basic solutions. In addition, the mechanical mixtures of IrO_2 and CuO were prepared; however, no improvement in OER activity (see Fig. S11†) through mechanical mixing was observed. The η at $j = 10$ mA cm⁻², the Tafel slopes and the mass activities at specific overpotentials in all of the prepared materials are shown in Table S4.† From this table, we can conclude that the Cu doping did enhance the OER activity, and $x = 0.3$ showed an excellent performance, which was consistent with the results from the relevant physical characterisations and DFT calculations.

Conclusions

The relevant experimental and theoretical results clearly showed that the d orbital occupation states of Ir-5d ($t_{2g}^5e_g^0$) in IrO_2 can be tuned by substituting Ir for Cu to create a d_z^2 -antibonding orbital (*i.e.*, one of e_g -antibonding orbitals) that is partially occupied in the $\text{Cu}_{0.3}\text{Ir}_{0.7}\text{O}_\delta$ composition. The $\text{Cu}_{0.3}\text{Ir}_{0.7}\text{O}_\delta$ composition exhibited an unexpected OER activity from its Tafel slope to its mass activity in three different pH solutions compared to IrO_2 . The substitution with Cu into the rutile structure of IrO_2 inherently had a strong Jahn–Teller effect due to the CuO_6 octahedron and induced partial oxygen defects in the lattice that changed the IrO_6 octahedral geometric structure and also lifted degeneracy of the t_{2g} and e_g orbitals. Therefore, the proposed method of doping with foreign elements to tune the electron occupation between the t_{2g} and e_g orbital states of Ir sites can yield an opportunity to design effective OER catalysts using TMO group materials.

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