An efficiently tuned d-orbital occupation of IrO_2 by doping with Cu for enhancing the oxygen evolution reaction activity†

Wei Sun,a Ya Song,b Xue-Qing Gong,*b Li-mei Caoa and Ji Yang*a

The oxygen evolution reaction (OER) at the anode is the 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 IrO_2 as a model because it is universally accepted as a current state-of-the-art OER catalyst. In this study, copper-doped IrO_2, particularly Cu_0.3Ir_0.7O_2, is shown to significantly improve the OER activity in acidic, neutral and basic solutions compared to un-doped IrO_2. The substituted amount of Cu in IrO_2 has a limit described by the Cu_0.3Ir_0.7O_2 composition. We determined that the performance of Cu_0.3Ir_0.7O_2 is due primarily to an increase in the Jahn–Teller effect in the CuO_6 octahedra, and partially to oxygen defects in the lattice induced by the IrO_6 octahedral geometric structure distortions, which enhance the lift degeneracy of the t_{2g} and e_g orbitals, making the d_3^2 orbital partially occupied. This phenomenon efficiently reduces the difference between ΔG_2 and ΔG_3 in the free energy from the density functional theoretical (DFT) calculations and can yield a lower theoretical overpotential comparable to that of IrO_2. 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.

Introduction

The oxygen evolution reaction (OER) at the anode is the key half reaction for splitting water into H_2 fuel and reducing the CO_2 concentration in fuels (e.g., CO, CH_4) 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.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 (d^0 ~ d^{10}),7 particularly t_{2g} and e_g, which can be systematically modified to optimize the catalytic activity at the surface.8–11 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.13–14 Numerous studies show that introducing F,15 Ru,16 Pd17,18 Ta19 and Zn20 into IrO_2 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 IrO_2, particularly in the Cu_{0.3}Ir_{0.7}O_6 composition, exhibits a high OER activity in acidic, neutral and basic solutions (pH ~ 1, 7 and 13, respectively). We chose IrO_2 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 (3d^{10}4s^1), and Cu^2+ is widely applied in superconductors.28–30 In this study, the Cu that is introduced into the IrO_2 lattice changes the IrO_2 lattice parameters and further affects the d-orbital distributions of the Ir-5d electrons; these mechanisms are discussed in detail. We also attribute the...
high performance observed to the fact that the doped Cu changes the Ir site electron structure and lifts its $e_g$ orbital resulting in partial occupation of its $d_{xz}$ orbital.

**Results and discussion**

Cu$_x$Ir$_{1-x}$O$_y$, with varying compositions, was synthesized hydrothermally via doping different amounts of Cu into the IrO$_2$ lattice, and allowing crystallization at 600 °C (detailed synthesis information is shown in the ESI†).

Fig. 1a shows the electrochemical characterization of the Cu$_{0.3}$Ir$_{0.7}$O$_5$ composition, which exhibited an excellent OER activity in three solutions with different pH values. The η requirements at $j = 10$ mA cm$^{-2}$, which is a meaningful reference due to its relevance to solar synthesis, were remarkably small at 351 mV in the acidic solution, 623 mV in the neutral solution and 415 mV in the basic solution, which indicated the excellent performance of Cu$_{0.3}$Ir$_{0.7}$O$_5$ in the acidic and neutral solutions; the values were much smaller compared to some reported for effective Co-based catalysts.$^{32-35}$ The excellent performance of Cu$_{0.3}$Ir$_{0.7}$O$_5$ was confirmed by measuring the Tafel slope to be $\sim$63 mV per dec in the acidic solution, $\sim$203 mV per dec in the neutral solution and $\sim$105 mV per dec in the basic solution. The stability of the prepared Cu$_{0.3}$Ir$_{0.7}$O$_5$ was evaluated by conducting chronoamperometry at 1.68 V (vs. RHE) for 6000 s, the results of which are shown in Fig. 1b. In each run, the normalized current slightly decreased due to oxygen bubbles accumulating on the surface, while the CV curves (Fig. 1b insert) before and after 6000 s are almost identical showing that the catalyst remains stable during the OER experiments.

As revealed by nitrogen adsorption isotherms (BET m$^2$ g$^{-1}$), the prepared catalysts have similar surface areas of 22–30 m$^2$ g$^{-1}$ (Table S1†). The compositions were characterized by EDS and the spectra are shown in Fig. S1† additional results were listed in Table S2.† Transmission electron microscopy (TEM) showed that Cu-doped IrO$_2$ had a short rod-like morphology structure that was different from the IrO$_2$ grain morphology (Fig. S2†); this was confirmed by scanning electron microscopy (SEM), as shown in Fig. S3.† It should be noted that the doping with Cu could change the IrO$_2$ lattice; thus, we have investigated how Cu doping can affect the IrO$_2$ rutile structure. The composition was shown to be maintained; its rutile structure at $x = 0–0.3$ and, when doped, at $x > 0.3$, it was found to be a mixture made up of CuO and partially doped IrO$_2$. X-ray diffraction (XRD, Fig. 2a) shows the diffraction planes (002) and (111) corresponding to CuO, which peak near $x = 0.3$, begin very weakly and increase gradually as more Cu is added, indicating that $x = 0.3$ is the maximum concentration for solid solution formation. It was also found that Ir could not insert into the CuO lattice even at a 10% molar ratio due to the different crystal

![Fig. 1](image1.png)

**Fig. 1** OER activity of Cu$_{0.2}$Ir$_{0.8}$O$_2$ in three solutions of different pH. (a) Tafel curves of Cu$_{0.2}$Ir$_{0.8}$O$_2$. The $R_j$ in the three solutions was $\sim$18 Ω (acidic), $\sim$15 Ω (neutral) and $\sim$28 Ω (basic), respectively. (b) Chronoamperometric curves at the constant potential 1.68 V vs. RHE. The inset shows the polarization curves for Cu$_{0.2}$Ir$_{0.8}$O$_2$ at the initial time point and after the chronoamperometric experiments. The catalyst loadings were 0.2 mg cm$^{-2}$ on a Ti plate.

![Fig. 2](image2.png)

**Fig. 2** (a) XRD patterns of the Cu$_x$Ir$_{1-x}$O$_5$ compositions with different amounts of Cu doping. (I)–(III) correspond to the (a) selected areas. (b) Polyhedron picture of one IrO$_2$ cell.

![Fig. 3](image3.png)

**Fig. 3** (a) Normalized Cu-K edge XANES spectra for Cu$_x$Ir$_{1-x}$O$_5$ compositions. (b) Shows the shakedown transition and the inset is a diagram of the Cu-4p orbital energy in two different symmetries. (c) Shows the amplified pre-edge region and the inset diagram shows the energy level of possible transitions. (b) and (c) correspond to the selected areas, I and II, in (a).
The Cu absorption near-edge structure (XANES), as shown in Fig. 3a.

(c) Pattern of the ratio of $S_1/S_2$ and $S_3/S_4$ versus the doped amount $x$.

Fig. 4 (a) XPS spectra of Cu-2p in the Cu$_x$Ir$_{1-x}$O$_2$ 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 Cu$_x$Ir$_{1-x}$O$_2$ compositions. (c) Pattern of the ratio of $S_1/S_2$ and $S_3/S_4$ versus $x$.

Fig. 5 (a) XPS spectra of Ir-4f in Cu$_x$Ir$_{1-x}$O$_2$ compositions. The solid vertical lines correspond to the Ir-4f$_{7/2}$ and 4f$_{5/2}$ peak positions of IrO$_2$. (b) Normalized Ir-LIII edge XANES spectra for Cu$_x$Ir$_{1-x}$O$_2$ compositions. (c) Second derivatives of Ir-LIII edge XANES spectra for Cu$_x$Ir$_{1-x}$O$_2$ 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. 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. 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. 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, 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 equal$^{42}$ (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$_6$ 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)$^{34,44}$ 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
neutrality to retain no net charge in the crystal structure; this produces a vacancy. These vacancies are identified and labeled as $\beta$ in the O-1s core level spectrum shown in Fig. 4b. Fig. 4a shows the Cu-2p core level spectrum of the doped materials and that of CuO for reference (detail in Fig. S8†). It is clearly noted that two de-convoluted peaks were identified and labeled as 1 and 2 at $2p_{3/2}$ in the doped material at $x = 0.1$ and 0.3; this finding indicated that two different states of the doped Cu corresponded to high and low valence states, respectively. The binding energy of peak 2 was marginally above that of the CuO sample, perhaps corresponding to the $O_{1s}$ state of the IrO$_6$ octahedron.

The electronegativity of Cu (i.e., the Pauling electronegativity is 1.9) is below that of Ir (i.e., the Pauling electronegativity is 2.2), meaning that oxygen is more inclined to gain an electron from copper. This was also confirmed by the O-1s XPS spectra; the primary peak labeled $\alpha$ originated from the metal (Cu, Ir)–O bond in the lattice, and the binding energy progressively decreased with the increasing Cu concentration. The ratio of $S_1/S_2$ and $S_0/S_2$ (i.e., S-peak area) versus the doped amount $x$ is shown in Fig. 4c. It was noted that the variation of $S_1/S_2$ and $S_0/S_2$ in Cu$_{1-x}$Ir$_x$O$_3$ showed a similar tendency as the doping amount increased but remained below $x \leq 0.7$; this indicated that there was a strong relationship between the low valence state of the doped Cu and that of the Vo. Thus, we inferred that the oxygen defects were generally closer to the Cu sites. As discussed above, the $c$-axis of a unit cell with doped Cu was reduced and was directly related to the planar oxygen in the octahedron. Thus, we inferred that the lattice oxygen defects might occur in the plane of the CuO$_6$ octahedron rather than at the apical location and that the defect position corresponded to the apical O of the IrO$_6$ octahedron.

This study then investigated how the modified IrO$_2$ doped by Cu affects the electronic structure of the Ir site. As shown in Fig. 5a (Ir-4f XPS), a shift to a lower binding energy was clearly observed in the doped samples compared to IrO$_2$, suggesting a higher electron density at the Ir site. We thus did not assign a low valence to Ir in all samples (see discussion in Fig. S9†). The performed Ir-L III edge XANES (Fig. 5b) revealed that an increasing number of Ir-5d states were occupied with IrO$_2$ doped at $x = 0.3$ with Cu due to a significant decrease in intensity in the so-called “white line region”. The edge positions of the Ir-L III edge for all of the prepared materials were found to be similar, indicating no valence change on Ir. In the ionic model, the five 5d electrons of the Ir$^{4+}$ ion in IrO$_2$ were shown to...
occupy the $t_{2g}$ triplet (i.e., $d_{xz}$, $d_{yz}$ and $d_{xy}$) and leave the higher $e_g$ doublet (i.e., $d_{xy}$ and $d_{z^2}$) empty under the octahedral crystal field described by the $t_{2g}$ $e_g$ configuration.\textsuperscript{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.\textsuperscript{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 2$p$ → $t_{2g}$ (5$d$) transition were increased above those of the 2$p$ → $e_g$ (5$d$) transition, which are in contrast to the findings in iridate perovskites;\textsuperscript{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.\textsuperscript{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.\textsuperscript{†} The colored region of Fig. 6a labels $\alpha$, $\beta$, $\gamma$, $\varepsilon$ and $\varphi$ for Ir–O $\alpha_{1g}$ bonding, $\sigma$ bonding, $\pi$ bonding, $\pi$ antibonding (including the non-bonding part) and $\sigma$ antibonding, respectively.\textsuperscript{46,53,54} One of the features of DOS is that the $\sigma$ and $\pi$ 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 $\sigma$ 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 $\pi$ 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 $\sigma$ bond to a $e_g$ orbital facilitates bonding with oxygen intermediates compared to a $\pi$ bond $t_{2g}$ orbital due to the $e_g$ orbital’s stronger overlap with O-2$p$.\textsuperscript{52,53} Synthich et al.\textsuperscript{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 Nørskov\textsuperscript{56} 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.\textsuperscript{†} The binding free energies of all the reaction intermediates (HO$^*$, O$^*$, HOO$^*$) involved in Fig. S9\textsuperscript{†} 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 $\Delta G_2 + \Delta G_3 = 3.2 \pm 0.2 \text{ eV}$.\textsuperscript{30,56} As a result, the catalysts have been
optimized, evidenced by the reduction in the difference between $\Delta G_2$ and $\Delta G_3$. It was found that the sum of $\Delta G_2$ and $\Delta G_3$ met this relationship for IrO$_2$ (3.22 eV), Ir$_{0.9}$Cu$_{0.1}$O$_6$ (3.17 eV) and Ir$_{0.7}$Cu$_{0.3}$O$_6$ (3.15 eV). In the case of IrO$_2$ ($t_{2g}^3e_g^0$), 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 $\sigma^*$ 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 than 1.68 eV of IrO$_2$); however, the difference between $\Delta G_2$ and $\Delta G_3$ 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 ($\eta_{the}(x = 0.3) = 0.39$ eV with $\eta_{the}(x = 0) = 0.51$ eV). The experimental data of OER for the studied catalysts are shown in Fig. 7b–d, which show that, except for Cu$_{0.3}$Ir$_{0.7}$O$_6$, all doped materials exhibited some OER activity; the Cu$_{0.4}$Ir$_{0.6}$O$_6$ and Cu$_{0.3}$Ir$_{0.7}$O$_6$ 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 was observed. The Tafel slopes and the mass activities at specific pH solutions compared to all of the prepared materials are shown in Table S4.† From this table, we can conclude that the Cu dopant 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-5$d$ ($t_{2g}^3e_g^0$) in IrO$_2$ can be tuned by substituting Ir for Cu to create a $d_2^2$-antibonding orbital (i.e., one of $e_g$-antibonding orbitals) that is partially occupied in the Cu$_{0.3}$Ir$_{0.7}$O$_6$ composition. The Cu$_{0.3}$Ir$_{0.7}$O$_6$ 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.

**Acknowledgements**

This research is based on work supported by the National Natural Science Foundation of China (21177037, 21277045, 21322307), the Public welfare project of the Ministry of Environmental Protection (201309021), the “Shu Guang” project of the Shanghai Municipal Education Commission and the Shanghai Education Development Foundation, and the Fundamental Research Funds for the Central Universities. We would like to thank beamline BL14W1 (Shanghai Synchrotron Radiation Facility) for providing the beam time.

**Notes and references**