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# Interface catalytic regulation *via* electron rearrangement and hydroxyl radicals triggered by oxygen vacancies and heavy metal ions†

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Although the enhanced intrinsic activities of some nano-metal oxides are obtained by manufacturing oxygen vacancies (OVs), the effect of multiple roles of OVs is ambiguous. Herein, an interface catalytic regulation *via* electron rearrangement and hydroxyl radicals ( $\cdot\text{OH}$ ) was proposed with the designed  $\text{ZrO}_2$  hollow sphere rich in OVs ( $V_{\text{O}}$ -rich  $\text{ZrO}_2$ ). Surprisingly, it was shown that the catalytic ability of  $V_{\text{O}}$ -rich  $\text{ZrO}_2$  was 9.9 times higher than that of  $\text{ZrO}_2$  with little OVs in electrochemical catalytic reduction of  $\text{Pb(II)}$ . It was found that the generation of  $\text{Zr}^{2+}$  and  $\text{Zr}^{3+}$  caused by OVs results in the rearrangement of abundant free electrons to facilitate the catalytic reaction rates. The longer bond length between  $V_{\text{O}}$ -rich  $\text{ZrO}_2$  and reactants, and the lower adsorption energy are beneficial for reactants to desorb, improving the conversion rates. Besides, the produced  $\cdot\text{OH}$  were captured which were induced by OVs and trace divalent heavy metal ions in *in situ* electron paramagnetic resonance (EPR) experiments, contributing to lowering the energy barriers. This study not only revealed the enhanced interface catalytic effect of electron rearrangement and generated  $\cdot\text{OH}$  triggered by OVs, but also provided unique insights into interface catalytic regulation on nano-metal oxides simulated by OVs.

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## 1 Introduction

Nano-metal oxide catalysts offering intriguing properties and stability, and low price are the subject of intense investigation, particularly in the energy and environment-related catalysis field.<sup>1–4</sup> However, some nano-metal oxides, like  $\text{TiO}_2$ ,  $\text{CeO}_2$ , and  $\text{ZrO}_2$ , suffer from poor catalytic efficiency due to their low electron transfer rates and limited active sites, greatly restricting their application.<sup>5–8</sup> To this end, manufacturing oxygen vacancies (OVs) on them is a simple and convenient way to enhance their intrinsic catalytic properties, which aroused tremendous interest.<sup>9–11</sup> For example, Pei *et al.*<sup>12</sup> used  $\text{TiO}_2$ , which possesses low conductivity and poor reactivity, to fabricate reductive  $\text{TiO}_{2-x}$  nanocrystals by self-doping with abundant OVs and achieve excellent catalytic activity in the oxygen reduction reaction (ORR). Sun *et al.*<sup>6</sup> reported that  $\text{CeO}_2$  with

rich OVs exhibited excellent conductivity and adsorption capacity, leading to satisfactory catalytic performance in the electrochemical reduction reaction.

It has been reported that the created OVs could play a significant role in catalysis. For instance, OVs serve as active sites for chemically absorbing the reactants, improving the number of reactants. Also, OVs could capture surrounding electrons to interact with intermediates with strong affinity and transfer electrons to them, boosting the redox reaction rates. Besides, the introduction of OVs changes the chemical environment and electronic structure of nano-metal oxides, modulating the band structure.<sup>13</sup> However, the detailed interface catalytic mechanisms between the oxygen-defective nano-metal oxides and reactants induced by OVs were still unclear and insufficient. Therefore, taking advantage of OVs for interface catalytic regulation and revealing their roles in catalytic reactions are necessary and important.

What's more, it has been reported that OVs are beneficial for the generation of some reactive oxygen species (ROS), and the participation of these ROS in the catalytic process remarkably improved the catalytic efficiency.<sup>14</sup> For example, Lyu *et al.* found that  $\text{O}_2$  could be directly activated into singlet oxygen ( $^1\text{O}_2$ ) or superoxide radicals ( $\text{O}_2^{\cdot-}$ ) spontaneously on  $\text{TiO}_{2-x}$ , exhibiting excellent performance in dye degradation, ORR, and cell viability.<sup>15</sup> Yuan *et al.*<sup>16</sup> presented  $\text{BiO}_{2-x}$  nanosheets rich in OVs to modulate ROS, catalyzing the production of  $\text{O}_2^{\cdot-}$  and  $\cdot\text{OH}$  in

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cancer cells. Also, it was found that OVs are well suited to ROS catalytic kinetics. Li *et al.*<sup>17</sup> found that the fabricated OVs on the surface of BiOCl are conducive to the formation of  $\cdot\text{O}^{2-}$ , achieving complete visible light NO oxidation with excellent efficiency. However, the research on ROS induced by OVs participating in catalytic reactions is mainly focused on biocatalysis, photocatalysis, *etc.* Relevant studies on electrocatalysts are few, although there is a great possibility that ROS would be produced and exist during the process.<sup>18</sup>

As a p-type semiconductor with a wide band gap (about 5 eV), the low catalytic activity of  $\text{ZrO}_2$  in the electrochemical process has been reported.<sup>19,20</sup> Also, it can be used as a raw material for ceramic glaze because of its strong chemical inertness, improving the chemical stability, and acid and alkali resistance of glaze.<sup>21,22</sup> Therefore, fabricating OVs in  $\text{ZrO}_2$  also has a great possibility for improving its intrinsic properties, broadening its application as a catalyst. Besides,  $\text{ZrO}_2$  is a kind of transition metal oxide with variable valence states of metal elements, which is quite similar to the above-mentioned  $\text{TiO}_2$  and  $\text{CeO}_2$ . However, the introduction of OVs induces the generation of  $\text{Ti}^{3+}$  and  $\text{Ce}^{3+}$  in  $\text{TiO}_2$  and  $\text{CeO}_2$ , respectively, participating in the catalytic reaction; while not only  $\text{Zr}^{3+}$  but also  $\text{Zr}^{2+}$  would be probably produced in oxygen-defective  $\text{ZrO}_2$ , which is worth exploring. What's more, the possible generated ROS should also be studied during the electrochemical catalytic experiments.

In this work,  $\text{ZrO}_2$  nanomaterials with mesoporous hollow sphere structures were fabricated, and different oxygen vacancy concentrations in the pristine  $\text{ZrO}_2$  were modulated through calcining them in an oxidizing or reducing gas environment at high temperature, denoted as  $\text{V}_o$ -poor  $\text{ZrO}_2$  and  $\text{V}_o$ -rich  $\text{ZrO}_2$ . The difference in oxygen vacancy concentrations among these  $\text{ZrO}_2$  nanomaterials was confirmed by electron paramagnetic resonance (EPR), X-ray photoelectron spectroscopy (XPS), and extended X-ray absorption fine structure (EXAFS). Besides, the effect of electron rearrangement induced by the abundant OVs is also verified to promote the catalytic reaction. To investigate the relationship between the catalytic ability of  $\text{ZrO}_2$  materials and their oxygen vacancy concentrations, electrochemical reduction experiments were implemented. Surprisingly, the  $\text{ZrO}_2$  possessing the highest concentration of OVs ( $\text{V}_o$ -rich  $\text{ZrO}_2$ ) exhibited superior catalytic capacity. During electrochemical catalytic reduction of  $\text{Pb(II)}$ , the current density of 1.0  $\mu\text{M}$   $\text{Pb(II)}$  signals with  $\text{V}_o$ -rich  $\text{ZrO}_2$  is nearly 10 times higher than that of  $\text{ZrO}_2$  with the lowest oxygen vacancy concentrations ( $\text{V}_o$ -poor  $\text{ZrO}_2$ ). At the same time, *in situ* EPR spectra and DFT calculations were employed to prove the generation of  $\cdot\text{OH}$  triggered by OVs and trace divalent heavy metal ions, such as  $\text{Pb(II)}$ , boosting the catalytic efficiency. Moreover, the multiple roles of OVs in interface catalytic regulation for enhanced catalytic capacity of  $\text{V}_o$ -rich  $\text{ZrO}_2$  were also explored.

## 2 Results and discussion

### 2.1 Structural and surface characterization

For obtaining  $\text{ZrO}_2$  samples with different oxygen vacancy concentrations, pristine  $\text{ZrO}_2$ , possessing a small quantity of intrinsic OVs, was first synthesized through the hydrothermal

method. Then,  $\text{V}_o$ -poor  $\text{ZrO}_2$  and  $\text{V}_o$ -rich  $\text{ZrO}_2$  were acquired through calcining pristine  $\text{ZrO}_2$  in air or  $\text{Ar}/\text{H}_2$ , respectively. As pristine  $\text{ZrO}_2$  was partially reduced with the treatment of  $\text{Ar}/\text{H}_2$ , a decreased number of oxygen atoms in  $\text{V}_o$ -rich  $\text{ZrO}_2$  were obtained. In contrast, the oxidizing gas (air) caused pristine  $\text{ZrO}_2$  to gain oxygen atoms, leading to the formation of  $\text{V}_o$ -poor  $\text{ZrO}_2$ . The calcination treatment in reducing gas is also applicable for many other nano-metal oxides to create OVs,<sup>23,24</sup> which is quite convenient and effective. The corresponding morphological characterization results of  $\text{V}_o$ -poor  $\text{ZrO}_2$ , pristine  $\text{ZrO}_2$ , and  $\text{V}_o$ -rich  $\text{ZrO}_2$  are shown in Fig. 1a–c and S1, S2†. The transmission electron microscopy (TEM) images of pristine  $\text{ZrO}_2$  and  $\text{V}_o$ -rich  $\text{ZrO}_2$  showed distinct hollow sphere structures with a diameter of about 150 nm, and the hollow volumes of  $\text{V}_o$ -rich  $\text{ZrO}_2$  particles significantly increased compared to those in pristine  $\text{ZrO}_2$  particles. However, the morphology of  $\text{V}_o$ -poor  $\text{ZrO}_2$  changed obviously, and severe aggregation was observed. The lattice orientations of (101) and (−111) in  $\text{V}_o$ -rich  $\text{ZrO}_2$  particles were marked in high-resolution transmission electron microscopy (HRTEM) images (Fig. 1d–f). It is clear to see that the lattice fringes of  $\text{V}_o$ -poor  $\text{ZrO}_2$  in Fig. 1d were clearer and neater than that of the others as the OVs were occupied by the oxygen atoms when being calcined in air. The energy-dispersive spectrometer (EDS) images in Fig. S2† show that the order of the percentage of oxygen atoms was  $\text{V}_o$ -poor  $\text{ZrO}_2 >$  pristine  $\text{ZrO}_2 >$   $\text{V}_o$ -rich  $\text{ZrO}_2$ , which was consistent with their corresponding oxygen vacancy concentrations.  $\text{N}_2$  adsorption–desorption isotherm curves in Fig. S3† exhibited the types of hysteresis loops in the range of 0.3–1.0 ( $P/P_0$ ), showing that all of them possessed mesoporous structures, and  $\text{V}_o$ -rich  $\text{ZrO}_2$  had the largest surface areas compared to the others. The X-ray diffraction (XRD) spectra of these  $\text{ZrO}_2$  particles are displayed in Fig. 1g. The peaks in  $\text{V}_o$ -rich  $\text{ZrO}_2$  were in good agreement with the standard card of JCPDS NO. 80-2155 (tetragonal phase), while the monoclinic  $\text{ZrO}_2$  characteristic peaks (JCPDS NO. 86-1449) were coincident with peaks in  $\text{V}_o$ -poor  $\text{ZrO}_2$  which only exhibited a small proportion of tetragonal phase characteristics. Besides, the pristine  $\text{ZrO}_2$  particles were also dominated by the tetragonal phase, showing a small intensity of characteristic peaks of monoclinic  $\text{ZrO}_2$ .<sup>25</sup> A strong intensity of monoclinic  $\text{ZrO}_2$  characteristic peak was observed in  $\text{V}_o$ -poor  $\text{ZrO}_2$  as pure stoichiometric  $\text{ZrO}_2$  crystals are the monoclinic phase which is highly stable at room temperature, and it would be converted to the tetragonal phase above 1400 K while to the cubic phase above 2600 K. It was found that the tetragonal phase could exist at normal temperature by introducing defects, and  $\text{V}_o$ -poor  $\text{ZrO}_2$  possesses more monoclinic phases due to the decrease of the oxygen vacancy concentrations.<sup>26</sup> More details of crystalline phase transition were revealed by Raman spectra (Fig. S4†). The comparison of EPR signals provided evidence of different oxygen vacancy concentrations among  $\text{V}_o$ -poor  $\text{ZrO}_2$ , pristine  $\text{ZrO}_2$ , and  $\text{V}_o$ -rich  $\text{ZrO}_2$ , as shown in Fig. 1h. The signals generated by the unpaired electrons at the OVs ( $g = 2.00$ ) weakened sharply after heat treatment in air while strengthened in  $\text{Ar}/\text{H}_2$ , which verified that  $\text{V}_o$ -rich  $\text{ZrO}_2$  possessed the highest oxygen vacancy concentration while  $\text{V}_o$ -poor  $\text{ZrO}_2$  had the lowest.<sup>27,28</sup> The Fourier transform infrared (FT-IR) spectra



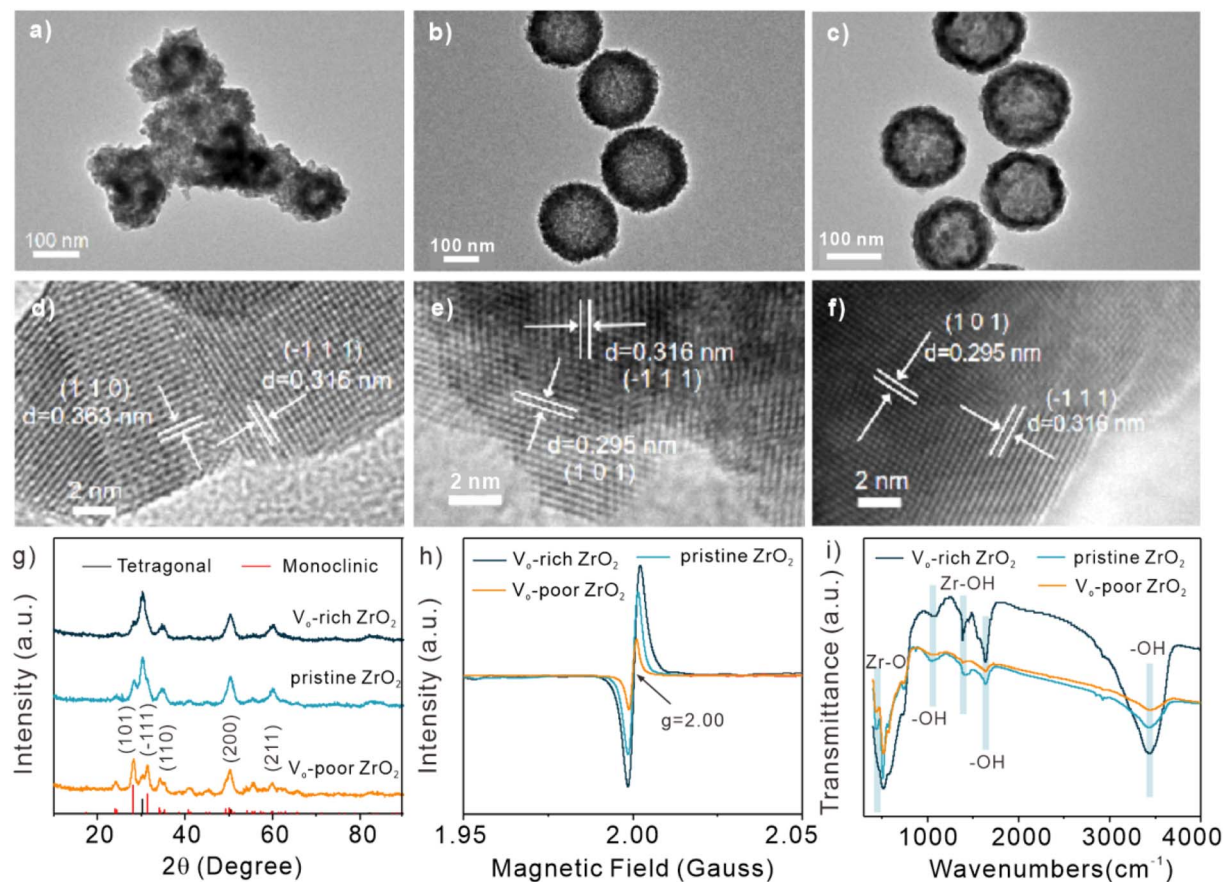


Fig. 1 (a–c) TEM and (d–f) HRTEM images of  $V_o$ -poor  $ZrO_2$ , pristine  $ZrO_2$ , and  $V_o$ -rich  $ZrO_2$ , respectively. The specific details of the (101), (–111), and (110) planes are marked in the images. Comparison of (g) XRD spectra, (h) EPR spectra, and (i) FT-IR spectra among  $V_o$ -poor  $ZrO_2$ , pristine  $ZrO_2$ , and  $V_o$ -rich  $ZrO_2$ .

(Fig. 1i) in the range of 400 to 4000  $cm^{-1}$  demonstrated that they all have five characteristic peaks and there is no significant difference in peak position. The small peaks at 475, 1080, and 1385  $cm^{-1}$  could be attributed to Zr–O vibration, bending vibration of hydroxyl groups, and Zr–OH vibration, respectively. The peaks at 1600 and 3430  $cm^{-1}$  were assigned to the –OH flexural vibration mode and tensile mode.<sup>29</sup> It was clearly shown that the content of –OH is also positively correlated with the concentration of OV and the –OH content in  $V_o$ -rich  $ZrO_2$  was much higher than that in pristine  $ZrO_2$  and  $V_o$ -poor  $ZrO_2$ .

## 2.2 Valence states and electronic structure study

For figuring out the valence states of Zr in the three samples with different concentrations of OV, the normalized Zr K-edge X-ray absorption near edge structure (XANES) spectra of Zr foil,  $ZrCl_4$ , pristine  $ZrO_2$ ,  $V_o$ -poor  $ZrO_2$ , and  $V_o$ -rich  $ZrO_2$  were analyzed, as shown in Fig. 2a. It is clear to see that the position of pre-edge peak tendency and the white line peak of Zr K-edge XANES in  $V_o$ -rich  $ZrO_2$  was in lower energy compared with that in pristine  $ZrO_2$  and  $V_o$ -poor  $ZrO_2$ , indicating that the valence states of Zr in  $V_o$ -rich  $ZrO_2$  were lower than those of the others, and all of them were lower than that in  $ZrCl_4$  ( $Zr^{4+}$ ). Besides, Fig. 2b demonstrated the fitting results of Zr K-edge EXAFS spectra of  $V_o$ -rich

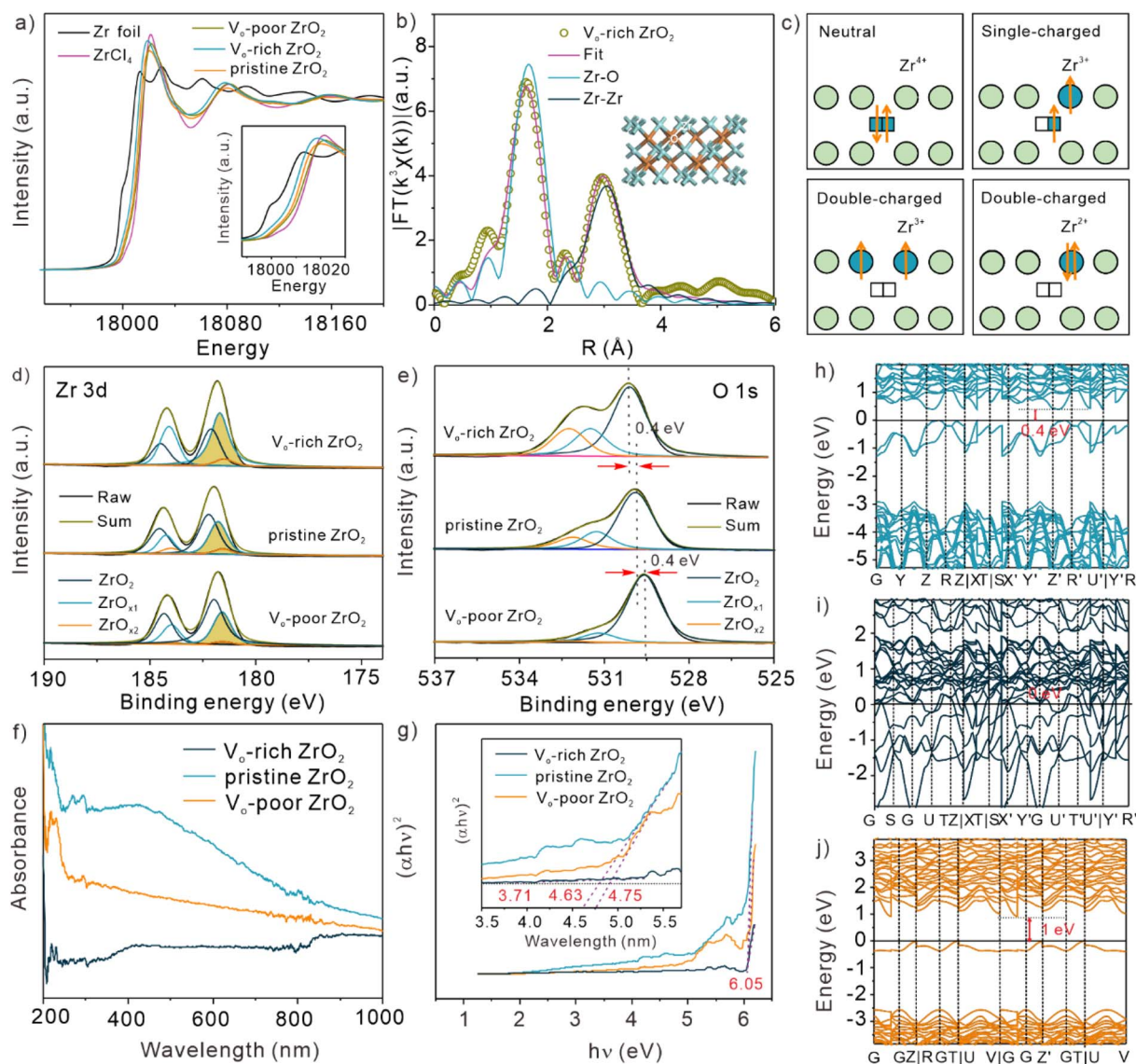
$ZrO_2$ , which showed that  $V_o$ -rich  $ZrO_2$  had Zr–O and Zr–Zr coordination peaks. More information is shown in Fig. S5, S6, and Table S1.† It was found that after calcining in 1 Ar/ $H_2$ , the coordination numbers of Zr–O in  $V_o$ -rich  $ZrO_2$  (3.1) decreased apparently compared to that in pristine  $ZrO_2$  (3.6) and  $V_o$ -poor  $ZrO_2$  (3.9), further proving the highest oxygen vacancy concentration in  $V_o$ -rich  $ZrO_2$ . There are three kinds of charge-characteristic OVs possibly generated in hypoxic  $ZrO_2$  due to Madelung potential, which are neutral, single, and double charge, respectively.<sup>26</sup> The corresponding schematic diagrams are shown in Fig. 2c. The oxygen atom escaped with two electrons remaining, resulting in the formation of neutral OVs; while single-charged OVs retain one electron, and the other one is transferred to the adjacent  $Zr^{4+}$  to generate  $Zr^{3+}$ . Regarding the double-charged OVs,  $Zr^{4+}$  is reduced to  $Zr^{3+}$  or  $Zr^{2+}$  depending on the number of electrons transferred.<sup>25</sup> The high-resolution X-ray photoelectron spectroscopy (XPS) spectra of Zr 3d (Fig. 2d) and O 1s (Fig. 2e) of the three  $ZrO_2$  samples were also analysed for exploring their different OV species. As shown in Fig. 2d, the peak at 182.1 eV was in the majority of Zr 3d in pristine  $ZrO_2$  (56.14%) and  $V_o$ -poor  $ZrO_2$  (61.04%), indicating that the  $Zr^{4+}$  was the main state present in these two  $ZrO_2$  samples. Besides, the peaks coloured with cyan and orange were the non-stoichiometric  $ZrO_2$  caused by OVs and assigned as  $ZrO_{x1}$  ( $1.5 < x1 < 2$ ) and  $ZrO_{x2}$



( $1 < x_2 \leq 1.5$ ), respectively. In Table S2,<sup>†</sup> we summarized the proportions of  $ZrO_{x_1}$ ,  $ZrO_{x_2}$ , and their sums in the total area of O 1s, as well as that in the total area of Zr 3d. It was obvious that the sum proportion of  $ZrO_{x_1}$  and  $ZrO_{x_2}$  in  $V_o$ -rich  $ZrO_2$  was much higher than that in pristine  $ZrO_2$  and  $V_o$ -poor  $ZrO_2$ , indicating that more single and double-charged OVVs were produced in  $V_o$ -rich  $ZrO_2$ . Similarly,  $ZrO_{x_1}$  and  $ZrO_{x_2}$  can be allocated to the position of 531.2 and 532.2 eV in the O 1s region in pristine  $ZrO_2$  and  $V_o$ -poor  $ZrO_2$ ,<sup>25,30</sup> as shown in Fig. 2e. It is worth noting that the peaks of  $ZrO_{x_1}$  and  $ZrO_{x_2}$  in  $V_o$ -rich  $ZrO_2$  were much obvious than that of the other two, which all verified the highest concentration of  $Zr^{2+}$  and  $Zr^{3+}$  in  $V_o$ -rich  $ZrO_2$ . And the peak at 529.9 eV in pristine  $ZrO_2$ , which was attributed to  $Zr^{4+}$ , shifted toward higher binding energy (530.2 eV) after fabricating

abundant OVVs while shifted toward lower binding energy (529.6 eV) in  $V_o$ -poor  $ZrO_2$ , indicating that more dramatic changes in the oxygen environment occurred.

To investigate the different electrochemical properties of these samples caused by OVVs, the cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) experiments on pristine  $ZrO_2$ ,  $V_o$ -poor  $ZrO_2$ , and  $V_o$ -rich  $ZrO_2$  were implemented. It was found that the conductivities of  $ZrO_2$  samples were positively correlated with the concentration of OVVs, as exhibited in Fig. S7.<sup>†</sup> Besides, the UV-vis absorption spectra of the three  $ZrO_2$  particles (Fig. 2f) were collected and converted to a Tauc plot (Fig. 2g) as there is a close relationship between band gap and electrical conductivity. The energy band gap was



**Fig. 2** (a) Normalized Zr K-edge XANES spectra of Zr foil,  $ZrCl_4$ , pristine  $ZrO_2$ ,  $V_o$ -poor  $ZrO_2$ , and  $V_o$ -rich  $ZrO_2$ . (b) Zr K-edge EXAFS spectra ( $R$  space,  $k^3$ -weighted) of  $V_o$ -rich  $ZrO_2$  and corresponding fitting curves. The inset image of (b) is coordination structure diagrams of  $V_o$ -rich  $ZrO_2$ . (c) Schematic diagram of four different forms of oxygen vacancies (electrons with oxygen vacancies indicated by up and down orange arrows). Comparison of high-resolution XPS spectra of (d) Zr 3d and (e) O 1s among pristine  $ZrO_2$ ,  $V_o$ -poor  $ZrO_2$ , and  $V_o$ -rich  $ZrO_2$ . (f) UV-vis DRS spectra, (g) Tauc plot obtained from the UV-vis data of pristine  $ZrO_2$ ,  $V_o$ -poor  $ZrO_2$ , and  $V_o$ -rich  $ZrO_2$ . Band gap diagrams of (h) pristine  $ZrO_2$ , (i)  $V_o$ -rich  $ZrO_2$ , and (j)  $V_o$ -poor  $ZrO_2$ .



calculated by converting the data according to the following formula:

$$(\alpha hv)n = k(hv - E_g) \quad (1)$$

where  $\alpha$  represents the absorption coefficient and  $hv$  is the photoelectron energy, and the value of  $k$  depends on the material. The characteristic value of a transition in a semiconductor is represented by two fixed values, denoted as  $n$ . For the direct transition, the value is 2 and for the indirect transition it is 1/2.<sup>31,32</sup> Among them, ZrO<sub>2</sub> belongs to the direct transition type and the intercept value was obtained by extending the straight part to the abscissa, which was the band gap energy ( $E_g$ ) of the semiconductor. The main band gap energy of all three samples was 6.05 eV, while the new band gap energies introduced by OV were 4.78, 4.92, and 3.71 eV for pristine ZrO<sub>2</sub>, V<sub>o</sub>-poor ZrO<sub>2</sub> and V<sub>o</sub>-rich ZrO<sub>2</sub>, respectively. This showed that it was OV that caused a sharp change in the energy band gap of the material which enhanced the transfer of electrons.<sup>27,33,34</sup> DFT calculations were also carried out to uncover the enhanced conductivity. After optimizing the configurations of ZrO<sub>2</sub> samples based on their different crystalline phases (Fig. S8†), a comparison of the total density of states (TDOS) and the corresponding band gap diagrams of pristine ZrO<sub>2</sub>, V<sub>o</sub>-rich ZrO<sub>2</sub>, V<sub>o</sub>-poor ZrO<sub>2</sub>, and ZrO<sub>2</sub> with no OV showed that the band gaps reduced obviously due to abundant OV existing in V<sub>o</sub>-rich ZrO<sub>2</sub>, which were 0.4, 0, 1, and 3.6 eV, respectively, as shown in Fig. 2h–j, S9, and S10.† Therefore, a conclusion could be drawn that abundant OV are key factors in the enhanced conductivity and electrochemical activity of V<sub>o</sub>-rich ZrO<sub>2</sub>.

### 2.3 Remarkable catalytic ability of V<sub>o</sub>-rich ZrO<sub>2</sub> triggered by OV

To explore the relationship between OV concentration and catalytic capacity, a divalent lead solution was adsorbed on the three ZrO<sub>2</sub> samples, revealing the interface catalytic effect between V<sub>o</sub>-rich ZrO<sub>2</sub> and lead ions. XAFS spectra of the three samples after adsorption of Pb(II) were first studied, which were denoted as pristine ZrO<sub>2</sub>/Pb, V<sub>o</sub>-poor ZrO<sub>2</sub>/Pb, and V<sub>o</sub>-rich ZrO<sub>2</sub>/Pb, respectively. Fig. 3a shows the normalized Pb L<sub>3</sub>-edge XANES spectra of Pb foil, PbO, pristine ZrO<sub>2</sub>/Pb, V<sub>o</sub>-poor ZrO<sub>2</sub>/Pb, and V<sub>o</sub>-rich ZrO<sub>2</sub>/Pb. It has been reported that the height of the white line peak is related to the electronic structure and usually a higher white line peak indicates a higher valence state. Surprisingly, the height of the white line peak of Pb in V<sub>o</sub>-rich ZrO<sub>2</sub>/Pb was similar to that in Pb foil, while that of pristine ZrO<sub>2</sub>/Pb and V<sub>o</sub>-poor ZrO<sub>2</sub>/Pb was between Pb foil and PbO, indicating that almost all Pb(II) was catalytically reduced to Pb(0) in V<sub>o</sub>-rich ZrO<sub>2</sub> while part of Pb(II) in pristine ZrO<sub>2</sub> and V<sub>o</sub>-poor ZrO<sub>2</sub>. It is worth mentioning that Pb(II) could be effectively reduced without an electric field, showing that V<sub>o</sub>-rich ZrO<sub>2</sub> had superb catalytic ability. Comparison of Pb 4f XPS spectra of V<sub>o</sub>-rich ZrO<sub>2</sub>/Pb(II) and Pb(NO<sub>3</sub>)<sub>2</sub> is shown in Fig. 3b. It was observed that the two peaks of Pb 4f<sub>7/2</sub> and Pb 4f<sub>5/2</sub> at 138.7 eV and 143.3 eV in V<sub>o</sub>-rich ZrO<sub>2</sub>, respectively, were a little lower than those in Pb(NO<sub>3</sub>)<sub>2</sub> (139.1 eV and 144.4 eV),<sup>35</sup> indicating that Pb(II) possibly obtained some electrons from V<sub>o</sub>-rich ZrO<sub>2</sub>,

which was in good agreement with the above XANES results. Besides, a comparison of XPS on different samples before and after the adsorption of Pb(II) was also performed. It is clear to see that the peak intensity of Pb 4f followed the trend as V<sub>o</sub>-rich ZrO<sub>2</sub> > pristine ZrO<sub>2</sub> > V<sub>o</sub>-poor ZrO<sub>2</sub>, as shown in Fig. S11,† indicating that V<sub>o</sub>-rich ZrO<sub>2</sub> had the largest amount of the adsorbed lead. At the same time, the surface energies of (101) and (−111) with different OV concentrations on V<sub>o</sub>-rich ZrO<sub>2</sub> have been calculated and the detailed information is shown in Table S2,† which indicated that with the increased concentration of OV, the surface energies of both facets increase, showing better adsorption abilities.<sup>36</sup> As there was a positive correlation between OV concentration and adsorption capacity, it could be deduced that the produced OV could increase the number of active sites on the surface of ZrO<sub>2</sub> to adsorb more Pb(II). Besides, the zeta potential test results in HAC–NaAc buffer solution at pH 5.0 are displayed in Fig. S12.† Clearly, as the concentration of OV increased, more free electrons covered the surface of ZrO<sub>2</sub>, resulting in a stronger electronegativity. Combined with the FT-IR results in Fig. 1i, perhaps more Pb(II) will be electrostatically adsorbed on V<sub>o</sub>-rich ZrO<sub>2</sub> as –OH could chemically bond and interact with Pb(II), resulting in better adsorption capacity toward Pb(II).<sup>29,37</sup> In addition, the changes of XPS Zr 3d and O 1s in V<sub>o</sub>-rich ZrO<sub>2</sub> were also investigated, as displayed in Fig. 3c, d and S13, S14.† Through the comparison, it was found that the total ratio of (ZrO<sub>x1</sub> + ZrO<sub>x2</sub>) decreased significantly after the adsorption of Pb(II) compared with that of pristine ZrO<sub>2</sub>/Pb(II) and V<sub>o</sub>-poor ZrO<sub>2</sub>/Pb(II), as shown in Table S3,† which indicated that Zr<sup>3+</sup> and Zr<sup>2+</sup> directly participated in boosting the catalytic reduction of Pb(II). For investigating the catalytic mechanisms of V<sub>o</sub>-rich ZrO<sub>2</sub> toward Pb(II) at the atomic level, the EXAFS spectra of Pb L<sub>3</sub>-edge in *R* space of pristine ZrO<sub>2</sub>/Pb, V<sub>o</sub>-poor ZrO<sub>2</sub>/Pb, and V<sub>o</sub>-rich ZrO<sub>2</sub>/Pb are exhibited in Fig. 3e, f and S15.† More detailed fitting results are shown in Table S4.† It was found that the first-shell coordination peak of V<sub>o</sub>-rich ZrO<sub>2</sub>/Pb was at  $R_{\text{Pb-O}} = 2.30 \text{ \AA}$  with 1.2 O atoms around,<sup>38</sup> where the second-shell coordination peak of V<sub>o</sub>-rich ZrO<sub>2</sub>/Pb was at  $R_{\text{Pb-Zr}} = 3.04 \text{ \AA}$  with 1.0 Zr atom around. Compared with pristine ZrO<sub>2</sub>/Pb and V<sub>o</sub>-poor ZrO<sub>2</sub>/Pb, the bond length of Pb–Zr in V<sub>o</sub>-rich ZrO<sub>2</sub>/Pb was much longer than that of them, which was 3.01 Å and 3.00 Å, respectively. It suggested that Pb ions adsorbed on V<sub>o</sub>-rich ZrO<sub>2</sub> were easier to desorb than that adsorbed on pristine ZrO<sub>2</sub> and V<sub>o</sub>-poor ZrO<sub>2</sub>, contributing to improving the interface catalytic efficiency.

### 2.4 The observed hydroxyl radicals induced by divalent heavy metal ions

The *in situ* EPR experiments were carried out to study the possibly produced ROS species during the electrochemical catalytic process with V<sub>o</sub>-rich ZrO<sub>2</sub>. Fig. 4a and b display the EPR spectra of observed ·OH under the specific experimental conditions, and 5,5-dimethyl-1-oxaphorphyrin-*N*-oxide (DMPO) was adopted as a spin-trapping agent. Obviously, it is clear to see that no matter whether Pb(II) and DMPO are added or not, there are no peak signals when without the effect of negative potential and the catalyst of V<sub>o</sub>-rich ZrO<sub>2</sub>. After applying the negative potential, no



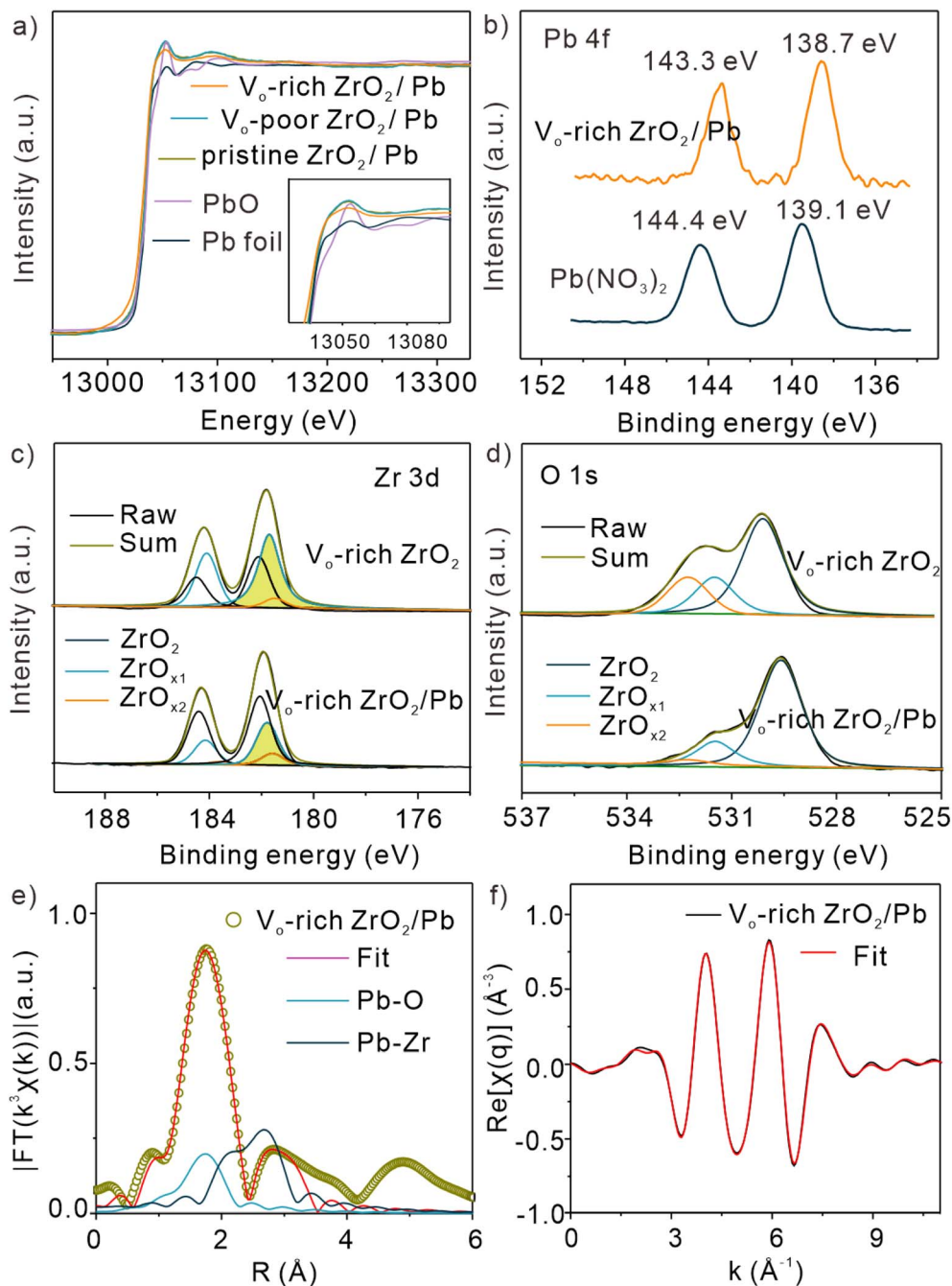


Fig. 3 (a) Normalized Pb  $L_{3}$ -edge XANES spectra of Pb foil, PbO, pristine  $ZrO_2/Pb$ ,  $V_o$ -poor  $ZrO_2/Pb$ , and  $V_o$ -rich  $ZrO_2/Pb$ . (b) Comparison of high-resolution Pb 4f XPS between  $V_o$ -rich  $ZrO_2/Pb$  and  $Pb(NO_3)_2$ . (c) High-resolution XPS of Zr 3d, (d) O 1s results of  $V_o$ -rich  $ZrO_2$  and  $V_o$ -rich  $ZrO_2/Pb$ . (e) Pb  $L_{3}$ -edge EXAFS spectra ( $R$  space,  $k^3$ -weighted) of  $V_o$ -rich  $ZrO_2/Pb$  and corresponding fitting curves. (f) The corresponding  $k^3(k)$  oscillations of  $V_o$ -rich  $ZrO_2/Pb$ .

EPR signals could be detected when there is no  $V_o$ -rich  $ZrO_2$  existing even though  $Pb(II)$  and DMPO were added. As shown in Fig. 4b, with the effect of negative potential and  $V_o$ -rich  $ZrO_2$ , several peaks appeared in the presence of  $Pb(II)$  and DMPO, while there were no peaks observed without the addition of  $Pb(II)$ . Interestingly, with the increasing concentration of  $Pb(II)$ , the typical peaks of DMPO- $\cdot OH$  (1:2:2:1) became more evident, indicating that a growing number of  $\cdot OH$  was produced during this electrochemical catalytic process. It is worth mentioning that

2,2,6,6-tetramethyl-4-piperidine (TEMP), another type of spin-trapping agent, was also solely added for excluding the possibility of the generation of other ROS species. In brief, it could be deduced that  $\cdot OH$  would be produced during the electrochemical catalytic reaction of  $V_o$ -rich  $ZrO_2$ , where  $Pb(II)$  is necessary and act as a radical initiator.

For figuring out whether other kinds of divalent heavy metal ions, except  $Pb(II)$ , could trigger the production of  $\cdot OH$ , 1.6  $\mu M$   $Cd(II)$  and  $Hg(II)$  were added respectively into the buffer solution



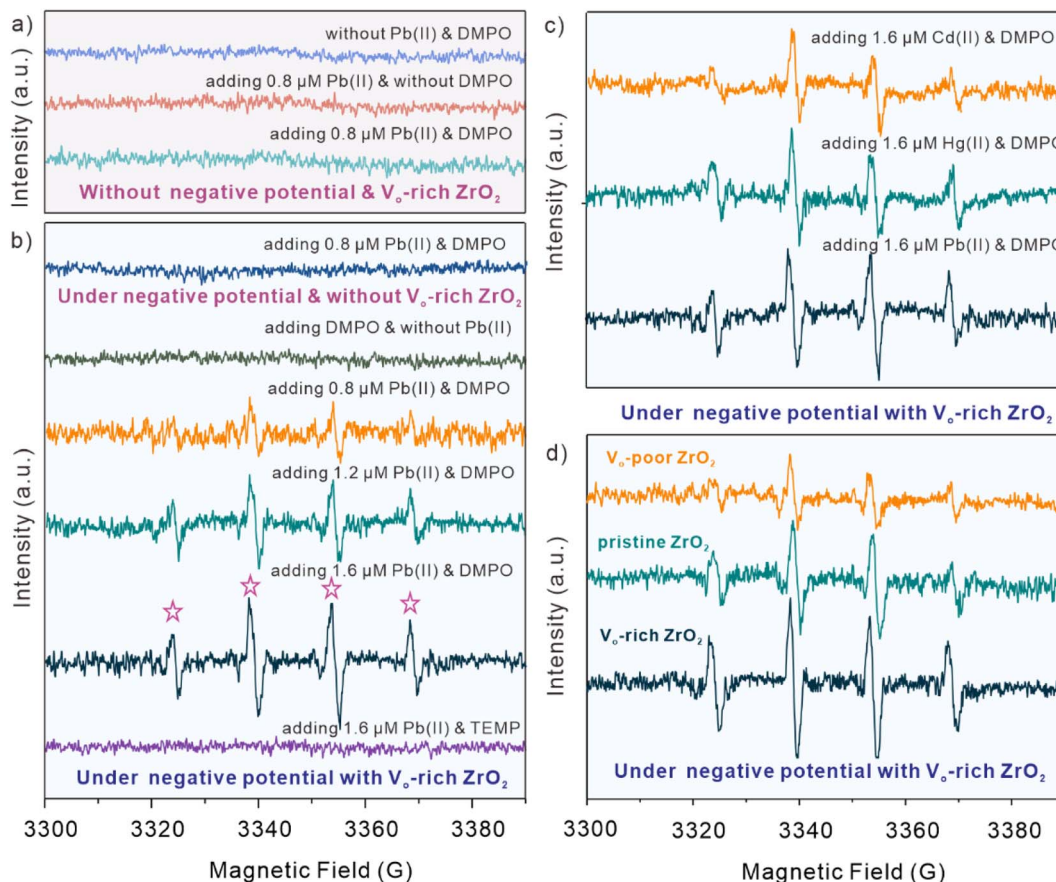


Fig. 4 (a) The obtained EPR spectra without negative potential and  $V_o$ -rich  $ZrO_2$ . (b) The obtained EPR spectra under negative potential. (c) Comparison of EPR spectra of  $V_o$ -rich  $ZrO_2$  in the presence of DMPO and 1.6  $\mu M$  different kinds of divalent heavy metal ions, including Cd(II), Hg(II), and Pb(II). (d) Comparison of EPR spectra of  $V_o$ -rich  $ZrO_2$ , pristine  $ZrO_2$ , and  $V_o$ -poor  $ZrO_2$  in the presence of DMPO and 2.0  $\mu M$  Pb(II).

under the same experimental conditions. Surprisingly, as displayed in Fig. 4c, the peaks of DMPO·OH were also detected when adding Cd(II) and Hg(II), while their intensities seemed a bit lower than that of adding Pb(II). This indicated that divalent heavy metal ions, not just confined to Pb(II), could induce the generation of ·OH with the electrochemical catalytic effect of  $V_o$ -rich  $ZrO_2$ . What's more, pristine  $ZrO_2$  and  $V_o$ -poor  $ZrO_2$  were also used to investigate the relationship between OV concentrations and the generated ·OH. Fig. 4c shows the comparison of EPR spectra of  $V_o$ -rich  $ZrO_2$ , pristine  $ZrO_2$ , and  $V_o$ -poor  $ZrO_2$  for electrochemical catalysis in the presence of DMPO and 2.0  $\mu M$  Pb(II). It was found that  $V_o$ -rich  $ZrO_2$  had the largest amount of produced ·OH during the reaction, and the intensities of DMPO·OH peak signals were positively correlated with the concentration of OVs. It could be concluded that the captured different intensities of DMPO·OH peak signals of these three samples were ascribed to their different concentration of OVs. And the generated ·OH perhaps have a specific impact on boosting the catalytic capacities of  $V_o$ -rich  $ZrO_2$ .

## 2.5 The investigation of changed electronic structure and energy barrier

DFT calculations were employed to further understand the inner mechanisms for obviously enhanced catalytic capacity of

$V_o$ -rich  $ZrO_2$  due to the generated abundant OVs. The electronic structure of  $V_o$ -rich  $ZrO_2$  after adsorption of Pb(II) was studied first. The optimized structures of Pb(II) adsorbed on the surface of the three  $ZrO_2$  samples are exhibited in Fig. S16.† It showed that the adsorption energies of Pb(II) on pristine  $ZrO_2$ ,  $V_o$ -rich  $ZrO_2$ , and  $V_o$ -poor  $ZrO_2$  were  $-1.542$ ,  $-0.196$  and  $-1.695$  eV. Apparently,  $V_o$ -rich  $ZrO_2$ /Pb had the lowest adsorption energy. The changes in the partial DOS of Zr, O, and Pb atoms in  $V_o$ -rich  $ZrO_2$  before and after the adsorption are shown in Fig. 5a. The degree of overlap between the orbitals of Pb 6p and Zr 4d near the Fermi level followed the trend as  $V_o$ -rich  $ZrO_2$ /Pb < pristine  $ZrO_2$ /Pb <  $V_o$ -poor  $ZrO_2$ /Pb (Fig. S17†), reflecting the opposite strength on desorption capacities. This evidence was in good agreement with the EXAFS results. Besides, it is clear to see that the electron density of Zr 3d and O 1s close to the Fermi surface increased a lot in  $V_o$ -rich  $ZrO_2$ /Pb, indicating that the intrinsic material becomes active when interacting with Pb atoms. A prominent newborn orbital hybrid peak (filled with purple) emerged in the partial DOS of O 1s of all three absorptive configurations, which proved the speculation that the adsorbed Pb atoms might take up the positions of OVs. Besides, the charge density difference images of the three adsorption structures showed that the electron cloud density (yellow area) around the Pb atoms in  $V_o$ -rich  $ZrO_2$ /Pb was the least while that



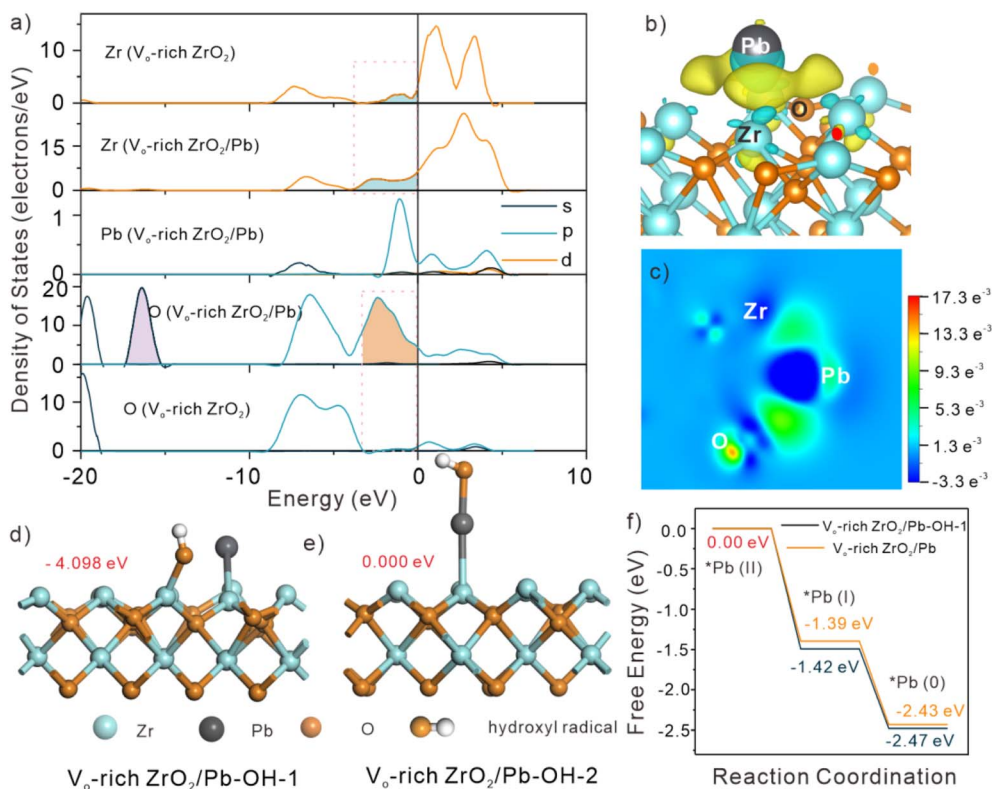


Fig. 5 (a) Comparison of DOS between  $V_o$ -rich  $ZrO_2/Pb$  and  $V_o$ -rich  $ZrO_2$ . (b) Charge density difference images of  $V_o$ -rich  $ZrO_2/Pb$ . The blue areas represent electron depletion, and the yellow areas represent electron accumulation. (c) Charge density difference image on the slice through Zr, O, and Pb atoms. The navy-blue areas represent electron depletion, and the green areas represent electron accumulation. (d and e) The two optimized configurations of  $V_o$ -rich  $ZrO_2/Pb$  when  $\cdot OH$  are participating in  $Pb(II)$  reduction. (f) Comparison of the free energy of reaction intermediates during the reduction process of  $Pb(II)$  on  $V_o$ -rich  $ZrO_2/Pb-OH-1$  and  $V_o$ -rich  $ZrO_2/Pb$ .

in  $V_o$ -rich  $ZrO_2/Pb$  was the largest, which further proved the low absorptive ability of  $Pb(II)$  on  $V_o$ -rich  $ZrO_2$ , as shown in Fig. 5b and S18.† The charge density difference image through Pb, Zr, and O atoms (Fig. 5h) displayed the electron flow condition that Zr atoms lost electrons to Pb atoms.<sup>39</sup> In other words, the electron rearrangement in  $V_o$ -rich  $ZrO_2$  caused by OVIs is beneficial for the catalytic reduction of  $Pb(II)$ . The Bader charge of Pb, Zr, and O atoms was computed, and the results are displayed in Fig. S19 and Table S5.† It was found that the adsorbed Pb could obtain  $0.167e$  more in  $V_o$ -rich  $ZrO_2$  than that in  $V_o$ -poor  $ZrO_2$ , which was conducive to boosting the reduction rates, showing the excellent catalytic ability of  $V_o$ -rich  $ZrO_2$ . The function of  $\cdot OH$  in catalysis of  $Pb(II)$  was also studied. According to different active sites of  $\cdot OH$  toward  $Pb(II)$ , two different optimized configurations of  $V_o$ -rich  $ZrO_2/Pb$  when  $\cdot OH$  participate in  $Pb(II)$  reduction are exhibited in Fig. 5d and e, which were denoted as  $V_o$ -rich  $ZrO_2/Pb-OH-1$  and  $V_o$ -rich  $ZrO_2/Pb-OH-2$ . Considering that  $ZrO_2/Pb-OH-1$  had the larger absorptive energy,  $-4.098$  eV, which had a more stable configuration, the energies for  $Pb(II)$  reduction on  $V_o$ -rich  $ZrO_2/Pb-OH-1$  were simulated. The reduction process of  $Pb(II)$  to  $Pb(0)$  was in two steps, as shown in Fig. 5f. Apparently, every step of  $V_o$ -rich  $ZrO_2/Pb-OH-1$  for  $Pb(II)$  reduction had lower energies than that of  $V_o$ -rich  $ZrO_2/Pb$ , indicating that the participation of  $\cdot OH$  was more conducive to the reaction.

## 2.6 Super-high catalytic capacity of $V_o$ -rich $ZrO_2$ in electrochemical reduction

For verifying the catalytic capacity and practical application prospect of  $V_o$ -rich  $ZrO_2$  in the electrochemical reduction

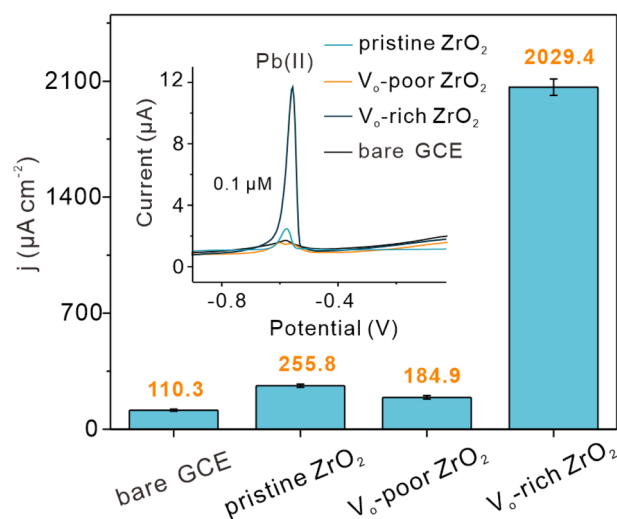


Fig. 6 Comparisons of the current densities and the SWASV curves of  $Pb(II)$  at the same concentration on the bare GCE and the three modified electrodes.





reaction, the three ZrO<sub>2</sub> samples were modified as catalysts on the same glassy carbon electrode (GCE) respectively for electrochemical catalysis of Pb(II) through square wave anode stripping voltammetry (SWASV). The bare GCE was also tested for comparison. The current responses of Pb(II) with increasing concentrations are shown in Fig. S20a–d.† Apparently, the current values of these modified GCEs toward Pb(II) at *ca.* –0.58 V all increased with the Pb(II) concentrations and an excellent linear relationship between Pb(II) concentration and peak current density was observed. The values of their current density per unit concentration were obtained by dividing the active area by the SWASV slope, and the active area of each modified electrode is shown in Fig. S21.† The current density per unit concentration of pristine ZrO<sub>2</sub>, V<sub>o</sub>-poor ZrO<sub>2</sub>, and V<sub>o</sub>-rich ZrO<sub>2</sub> modified electrodes toward Pb(II) was 255.8, 184.9, and 2029.4 μA cm<sup>-2</sup> μM<sup>-1</sup>, respectively, (Fig. 6). It was surprising that the catalytic ability of V<sub>o</sub>-rich ZrO<sub>2</sub> was almost 6.9 times higher than that of pristine ZrO<sub>2</sub> and even 9.9 times higher than that of V<sub>o</sub>-poor ZrO<sub>2</sub>, which indicated that the incredibly improved electrocatalytic ability of pristine ZrO<sub>2</sub> was obtained after creating OV. Besides, the order of their catalytic ability (V<sub>o</sub>-rich ZrO<sub>2</sub> > pristine ZrO<sub>2</sub> > V<sub>o</sub>-poor ZrO<sub>2</sub>) was consistent with their concentration of OV, implying the vital role of OV in the catalytic reduction of Pb(II). Besides, the corresponding experiments for characterizing catalytic cycle properties of V<sub>o</sub>-rich ZrO<sub>2</sub> have also been carried out, showing excellent practical application prospects. More information is displayed in Fig. S22.†

Fig. 7 vividly depicts the interface catalytic regulation *via* significant roles of OV in V<sub>o</sub>-rich ZrO<sub>2</sub> for enhancing the catalytic efficiency in the electrochemical reduction of Pb(II).

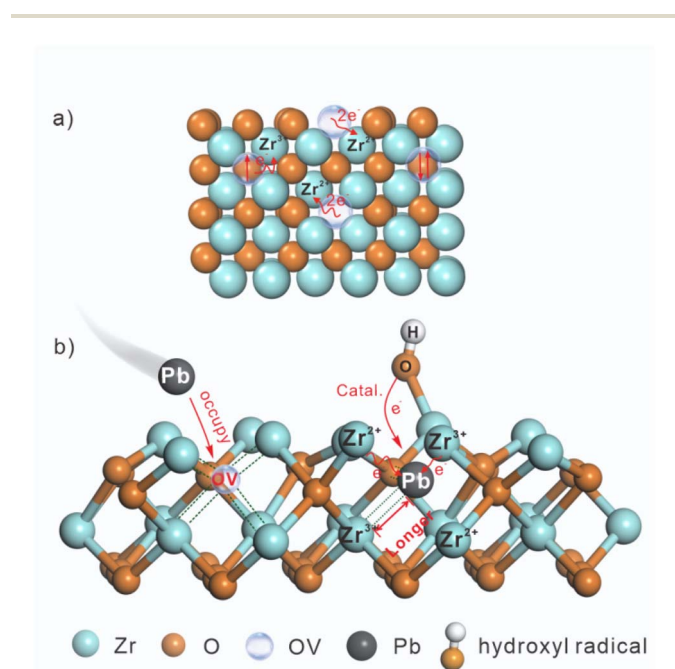


Fig. 7 The schematic diagram of (a) electron rearrangement on V<sub>o</sub>-rich ZrO<sub>2</sub> triggered by OV; (b) interface catalytic regulation *via* OV and ·OH on V<sub>o</sub>-rich ZrO<sub>2</sub>.

Fig. 7a shows that the extra electrons remaining in OV transferred to the adjacent Zr<sup>4+</sup>, leading to the generation of Zr<sup>3+</sup> and Zr<sup>2+</sup>. Then, more Pb(II) is adsorbed on the surface OV of V<sub>o</sub>-rich ZrO<sub>2</sub> due to the large surface area, occupying the position of OV and resulting in the formation of Pb–O and Pb–Zr bonds, as shown in Fig. 7b. The accumulated electrons in Zr<sup>3+</sup> and Zr<sup>2+</sup> directly transferred to Pb(II), promoting the catalytic reduction of adsorbed Pb(II) to Pb(0). Besides, the longest Pb–Zr bonds and the lowest adsorption energy in V<sub>o</sub>-rich ZrO<sub>2</sub>/Pb compared to those in pristine ZrO<sub>2</sub>/Pb and V<sub>o</sub>-poor ZrO<sub>2</sub>/Pb are beneficial for Pb(II) to desorb, improving the rates of conversion. What's more, the generated ·OH which are induced by OV and Pb(II) also act as redox mediators to accelerate the electron transfer rates in electrochemical reduction reactions, boosting the interface catalytic effect.

### 3 Conclusions

In summary, ZrO<sub>2</sub> mesoporous hollow spheres rich in OV were fabricated and the multiple roles of OV in interface catalytic regulation were revealed. First, the introduction of OV brings more catalytic reaction sites. After fabricating abundant OV, the adsorption capacity is improved due to increased surface area, and more surface –OH is produced for chemical interaction with reactants. Unlike other catalytic systems where OV are indirectly involved in catalytic processes, in this study, OV themselves are catalytic rooms for the adsorbed reactants, enhancing the rates of conversion and the reaction. Second, OV cause the rearrangement of electrons. The excess electrons in OV transfer to the adjacent Zr<sup>4+</sup>, promoting the formation of Zr<sup>2+</sup> and Zr<sup>3+</sup>, which in turn transfer electrons to the reactants. Zr<sup>2+</sup> and Zr<sup>3+</sup> serve as redox mediators, accelerating the electron transfer rates and boosting the catalytic reduction reaction. The changed electronic and energy band structures induced by OV also enhanced the intrinsic conductivity and activity of pristine ZrO<sub>2</sub>. Besides, DFT calculations and EXAFS revealed that longer Pb–Zr and lower absorptive energies are beneficial for desorption. Third, for the first time, ·OH have been observed to be triggered by OV and divalent heavy metal ions in *in situ* EPR experiments. It was shown that when adding divalent heavy metal ions, more produced ·OH were captured in the electrochemical reduction reaction with V<sub>o</sub>-rich ZrO<sub>2</sub>, which also act as a catalyst. In the experiments of electrochemical reduction of Pb(II), it was shown that the catalytic ability of V<sub>o</sub>-rich ZrO<sub>2</sub> was almost 9.9 times higher than that of V<sub>o</sub>-poor ZrO<sub>2</sub>, showing superior practical application prospects in the fields of chemistry, nanomaterials, catalysis, *etc.* This finding will provide enlightenment and guidance for wide communities including advanced *in situ* measurements, especially in the fields of chemistry, catalysis, nanomaterials, *etc.*, in boosting the catalytic effect through interface catalytic regulation.

### 4 Experimental section

#### 4.1 Synthesis of ZrO<sub>2</sub> hollow spheres

The synthesis of ZrO<sub>2</sub> hollow spheres referred to the previous literature with revision.<sup>40</sup> Zirconium dichloride (0.3 g) is added



to acetone (90 mL) and stirred magnetically for a few minutes to completely dissolve to form a colourless solution. The solution was immediately filled into a 100 mL Teflon-lined container, sealed, and placed in an oven at 200 °C for 12 h, and then naturally cooled down to room temperature. The resulting solution was centrifuged at 10 000 rpm for 3 minutes, then alternately washed twice with water, ethanol, and acetone. The obtained precipitate was freeze-dried all day, and the resulting powder was called pristine ZrO<sub>2</sub>.<sup>40</sup> The pristine ZrO<sub>2</sub> powder was calcined at 650 °C in a tube furnace with an average ramp rate of 3 °C min<sup>-1</sup> for 90 minutes, and the gas introduced was (Ar/H<sub>2</sub>, air); the products were named V<sub>o</sub>-rich ZrO<sub>2</sub> and V<sub>o</sub>-poor ZrO<sub>2</sub>.

## 4.2 Computational methods

Spin-polarized DFT calculations were performed using the Vienna *ab initio* simulation package (VASP).<sup>41,42</sup> The generalized gradient approximation proposed by Perdew, Burke, and Ernzerhof (GGA-PBE) is selected for the exchange-correlation potential.<sup>43</sup> The pseudo-potential was described by the projector-augmented-wave (PAW) method.<sup>44</sup> The geometry optimization is performed until the Hellmann-Feynman force on each atom is smaller than 0.02 eV·Å<sup>-1</sup>. The energy criterion is set to 10<sup>-6</sup> eV in the iterative solution of the Kohn-Sham equation. For DOS calculation, a 2 × 1 × 1 supercell adopted from tetragonal ZrO<sub>2</sub> was used for pristine ZrO<sub>2</sub> and V<sub>o</sub>-rich ZrO<sub>2</sub>, and a 1 × 12 × 1 supercell adopted from monoclinic ZrO<sub>2</sub> was used for V<sub>o</sub>-poor ZrO<sub>2</sub>. The supercell size for pristine ZrO<sub>2</sub> and V<sub>o</sub>-rich ZrO<sub>2</sub> is 10.14 × 5.07 × 5.07 Å<sup>3</sup>, and it is 5.1454 × 10.4150 × 5.3107 Å<sup>3</sup> for V<sub>o</sub>-poor ZrO<sub>2</sub>. The k-mesh for structure optimization is 0.06 2π Å<sup>-1</sup>. For adsorption calculation, a 2 × 2 supercell with 12 Å vacuum is applied. The size of V<sub>o</sub>-rich ZrO<sub>2</sub>/Pb and pristine ZrO<sub>2</sub> is 10.14 × 10.14 × 16.8022 Å<sup>3</sup>. The size of V<sub>o</sub>-poor ZrO<sub>2</sub>/Pb is 10.415 × 10.6214 × 17.0749 Å<sup>3</sup>. The k-mesh for structure optimization is 0.06 2π Å<sup>-1</sup>. The hydroxyl radicals were calculated using PBE and their charge states are automatically assigned by the program.

## Data availability

We have provided all the data in the manuscript and ESI.†

## Author contributions

X. H., M. Y. and X. X. designed this project. X. X. and C. Z. implemented the experiments. Z. S. implemented the DFT calculations. X. X., Y. Z. and Z. G. completed the data analysis. X. X. and C. Z. drafted the manuscript. S. C., P. L. and Y. S. reviewed and edited the manuscript. All authors approved the final version.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

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