Revealing the Role of d Orbitals of Transition-Metal-Doped Titanium Oxide on High-Efficient Oxygen Reduction

Fei Lu1,2†, Weiwei Xie3†, Yan Wang1, Fengchu Zhang1, Yong Xu4, Bo Zhou4, Shoujie Liu4, Xi Wang1* & Jiannian Yao2

1Department of Physics, School of Science, Beijing Jiaotong University, Beijing 100044, 2Key Laboratory of Photochemistry, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, 3Institute of Physical Chemistry, Karlsruhe Institute of Technology, Karlsruhe 76131, 4Chemistry and Chemical Engineering Guangdong Laboratory, Shantou 515031

*Corresponding author: xiwang@bjtu.edu.cn; † F. Lu and W. Xie contributed equally to this work.

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Precise catalysis is critical for the high-quality catalysis industry. However, it remains challenging to fundamentally understand precise catalysis at the atomic orbital level. Herein, we propose a new strategy to unravel the role of specific d orbitals in catalysis. The oxygen reduction reaction (ORR) catalyzed by atomically dispersed Pt/Co-doped Ti1−xO2 nanosheets (Pt1/Co1−Ti1−xO2) is used as a model catalyst. The z-axis d orbitals of Pt/Co–Ti realms dominate the O2 adsorption, thus triggering ORR. In light of orbital-resolved analysis, Pt1/Co1−Ti1−xO2 is experimentally fabricated, and the excellent ORR catalytic performance is further demonstrated. Further analysis reveals that the superior ORR performance of Pt1−Ti1−xO2 to Co1−Ti1−xO2 is ascribed to stronger activation of Ti by Pt than Co via the d–d hybridization. Overall, this work provides a useful tool to understand the underlying catalytic mechanisms at the atomic orbital level and opens new opportunities for precise catalyst design.

Keywords: transition-metal-doped titanium oxide, oxygen reduction reaction, orbital-resolved analysis, d–d hybridization, theory-driven catalyst design

Introduction

The sluggish kinetics, especially the kinetically hindered multielectron transfer process, has long posed one of the greatest challenges in electrocatalysis.1–3 Enormous efforts have been dedicated to design the new class of cost-effective and high-performance electrocatalysts.4,5 The pioneering works provide significant inspiration for the geometric and electronic structure regulation on catalysts.6–20 The geometric optimizations focus on tailoring crystal facets,6,7 refining surface strain,8–11 or downgrading into single-atom scale,12–14 while electronic-structure optimization pursues the regulation of charge transfer or d-band center.15–20 However, rational catalyst design via the regulation of d-orbital energies/orientations has been rarely reported, which requires a comprehensive understanding of the effects of each d orbital on catalysis (Figure 1a). To this end, three key

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questions are needed to be addressed: (1) How are the d orbitals of catalysts modulated by the local environment? (2) What is the role of d orbitals of catalysts in catalysis? and (3) How do we guide the rational catalyst design toward high-performance and precise catalysis?

Herein, we outline a new strategy to reveal the roles of individual d orbitals of catalysts in catalytic reactions. The method is illustrated in the oxygen reduction reaction (ORR) catalyzed by the atomically dispersed Pt–Ti–O nanosheet. Pt and Ti in close proximity, both with unsaturated coordination with five oxygens,21 may trigger the intensive d–d interaction,22,23 which is confirmed from the well-matched energy levels of Pt–5d and Ti–3d orbitals in the projected density of states (pDOS) profile (Figure 1c and Supporting Information Figure S1b). The charge density distribution further clarifies that the d–d hybridization increases the electron density in the catalytic unit (Figure 1d). Then, two intriguing questions arise: (1) Which d orbitals dominate the Pt–Ti interaction? and (2) Which d orbitals play the key role in ORR?

**Experimental Methods**

**Synthesis of monolayered Pt1–Ti1–xO2 nanosheets**

The cation-deficient Ti1–xO2 nanosheets were initially fabricated. In detail, Cs2CO3 (1.63 g) and anatase TiO2 (2.14 g) were ground and followed calcination at 800 °C for 20 h twice to produce the layered titanate Cs0.7Ti1.825□0.175O4 (□ represents Ti vacancy (Tivac)). Then, protonic titanate (H0.7Ti1.825□0.175O4) was obtained by the acid-exchange procedure with 1 mol L−1 HCl for three times (1 day per period), in which the liquid-to-solid ratio was maintained 100 mL g−1. Afterward, the products were washed by distilled water (18.2 MΩ) several times and vacuum-dried overnight at 80 °C. Finally, monolayered Ti1–xO2 nanosheets (in the colloidal state) were obtained via a soft-chemical exfoliation process by dispersion of the protonic titanate into 0.017 mol L−1 tetrabutylammonium (TBAOH) solution and shaken for 10 days at 220 rpm, in which the liquid-to-solid ratio was set to be 250 mL g−1.

Then, Pt1–Ti1–xO2 nanosheets were synthesized via an electrostatic adsorption-anchorage process by employing the obtained Ti1–xO2 nanosheets and Pt(NH3)4(OH)2 as anchored host and Pt precursor, respectively. The positively charged Pt2+ could be electrostatically adsorbed at the negatively charged Tivac site. Specifically, 1 mL Pt(NH3)4(OH)2 solution (0.96 mg mL−1) was dripped into 10 mL Ti1–xO2 colloidal with constant stirring. Finally, the Pt1–Ti1–xO2 nanosheets were obtained after centrifugation at 20,900 rpm and freeze-drying for 3 days.

**Synthesis of monolayered Co1–Ti1–xO2 nanosheets**

The Co1–Ti1–xO2 nanosheets were engineered via a doping-exfoliation strategy, according to the previous
reports. Initially, K₀.₅Ti₁.₇Li₀.₂Co₀.₁O₄ was fabricated by grind and calcination of K₂CO₃ (0.55 g), Li₂CO₃ (0.07 g), CoO (0.07), and rutile TiO₂ (1.36 g) at 1000 °C for 1 h, followed by a second grind and calcination of the previous-step product at 1000 °C for 20 h. Then, the K₀.₅Ti₁.₇Li₀.₂Co₀.₁O₄ undergoes the same acid-exchange, wash with distilled water, and exfoliation process in sequence to obtain Co₁−Ti₁−CoO₄ (accurately Ti₁.₇Co₀.₁O₄) with Co loading of ~3.9 wt %.

Characterizations

The microstructure of the catalysts was characterized by field-emission scanning electron microscopy (FE-SEM; SU8010; Hitachi, Tokyo, Japan) and transmission electron microscopy (TEM; JEM-2010; JEOL, Tokyo, Japan) operated at an accelerating voltage of 200 kV, and high-angle annular dark-filed scanning TEM (HAADF-STEM; Tecnai G2-F20; FEI, Oregon, USA). The paper was sent to the Demeter software package. The quantitative K₁,₂-edge and Co₁,₃-edge spectra were carried out with Athena and Artemis (Thermo Fisher Scientific, Massachusetts, USA). The UV-vis absorption was recorded on UV-2600 (Shimadzu, Osaka, Japan). The content of doped heteroatomic black to nanosheets was dispersed into the former nanosheet colloid to obtain a uniform suspension. Finally, the suspension was freeze-dried for 3 days to obtain the mixture. The obtained mixture (the weight ratio of carbon black to nanosheets is 25:75, 6 mg) was initially dispersed in 600 µL water/ethanol mixed solution (50:50 in volume ratio) containing 30 µL 5 wt % Nanox (Dupont) with a 60-min sonication to form a homogeneous ink. Then, 5 µL of the ink was deposited onto a glassy carbon rotating disk electrode (RDE; 0.07 cm², ALS Co., Ltd., Tokyo, Japan) serving as the working electrode. Meanwhile, graphite rod and Ag/AgCl serve as working and reference electrodes within the three-electrode system (CHI 760E, Chenhua, Shanghai, China), respectively. The electrolyte for the ORR test was O₂-saturated 0.1 M KOH solution. Linear sweep voltammograms (LSVs) were obtained at the varied rotation from 400–2500 rpm and the scan rate of 10 mV s⁻¹. The electron-transfer number (n) during the ORR process was calculated according to the Koutecky–Levich (K−L) equation:

\[
\frac{1}{J} = \frac{1}{J_L} + \frac{1}{J_K} = \frac{1}{Be^{1/2}} + \frac{1}{J_K}
\]

where, J and J_K are the measured current density and kinetic-limiting current density, respectively. ω is the electrode rotation rate.

\[
B = 0.62nFCDO_{2}^{2/3}ν^{-1/6}
\]

B could be determined from the slope of the K−L plots obtained from the aforementioned K−L equation. n is the number of transferred electrons during the ORR process, F is the Faraday constant (96,485 C mol⁻¹), C_O (1.2 × 10⁻⁶ mol cm⁻³) and D_O (1.9 × 10⁻⁵ cm² s⁻¹) are the concentration and diffusion coefficients of O₂ in electrolyte, and ω (0.01 cm² s⁻¹) is the kinematic viscosity of the electrolyte.

Computational methods

The spin-polarized density functional theory (DFT) calculations were performed using the Quantum ESPRESSO Package. The generalized gradient approximation with the Perdew–Burke–Ernzerhof-type exchange-correlation functional (GGA-PBE) and projector augmented wave (PAW) method were adopted in all the calculations with the kinetic energy cutoff of 80 Ry. A vacuum space of 15 Å was used to avoid the interaction between two periodic units along the z direction. The 2 × 3 × 1 k-point sampling was used for the 3 × 3 × 1 supercell of the TiO₂ nanosheet. The convergence of energy and force were set as 10⁻⁵ Ry and 10⁻⁴ Ry a.u⁻¹, respectively. For the orbital-resolved bonding analysis, we employed the crystal orbital Hamilton population (COHP) method. The PAW wave functions were projected onto atomic orbital basis functions using Wannier90 (v3.1.0). It is noted that the original d orbitals are aligned with the axes of the global coordinate system. However, the Ti−O and Pt−O bond

X-ray absorption fine structure measurements

X-ray absorption near-edge spectroscopy (XANES) and extended X-ray absorption fine structure (EXAFS) measurements at Pt L₃-edge and Co K-edge were performed at beamline 1W1B at Beijing Synchrotron Radiation Facility (SSRF). Pt foil and PtO₂ for Pt and Co foil, CoO, and Co₃O₄ for Co were employed as the reference samples. XAFS analyses on Pt L₃-edge and Co K-edge spectra were carried out with Athena and Artemis in the Demeter software package. The quantitative information were obtained by the least-squares curve fitting in the k²-weighted EXAFS oscillation in the range of 0–6 Å, using the ARTEMIS module of IFEFFIT (version 1.2.11, IFEFFIT, Copyright 2008, Matthew Newville, University of Chicago).

Electrochemical measurements

The as-prepared nanosheets were initially dispersed in water. Then, the carbon black, with a weight ratio of 1:4 to the nanosheets, was dispersed into the former

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axes form angles of ∼45° with the z axis of the global coordinate system. To correctly display the chemical bonding in terms of atomic orbitals, the d orbitals of Ti and Pt were rotated by an angle of 45° around the z axis of the global coordinate system.

The ORR performance of a Pt/Co-doped TiO₂ nanosheet was evaluated by computing the reaction-free energy defined as:

\[ \Delta G_{\text{H}} = \Delta E_{\text{H}} + \Delta E_{\text{ZPE}} - T \Delta S \]  

where \( \Delta E_{\text{ZPE}} \) and \( \Delta S \) are the differences in the zero-point energy and the entropy, respectively, between the adsorbed and the gas phases. \( \Delta E \) is the adsorption energy of \( X \) species (\( X = \text{O}_2, \text{OOH}, \text{O}, \text{and OH} \)) on Pt/Co-doped TiO₂ obtained by DFT calculations and is defined as:

\[ \Delta E = E_{\text{sub} + X} - E_{\text{sub}} - E_X \]  

Results and Discussion

To tackle these questions, we performed the COHP analysis, which serves as a chemical bonding indicator to measure the covalent bond strength for solids. Noteworthily, the chemical interpretation substantially depends on the orientation of its underlying atomic orbitals. To correctly display the chemical bonding in terms of atomic orbitals, the projection of d orbitals of Ti and Pt were rotated by an angle of 45° around the z axis of the global coordinate system. The COHP integral of the orbital-resolved COHP (Supporting Information Figures S1c and S1d) up to Fermi energy for the d-d hybridization. The overwhelmingly larger integrated crystal orbital Hamilton population (ICOHP) values of \( d_{yz}, d_{z^2}, \) and \( d_{xz} \) over \( d_{xy} \) and \( d_{x^2-y^2} \) orbitals indicate that the d orbitals along the z-axis of the global coordinate system make dominant contributions to Pt-5d and Ti-3d interaction. In other words, the d orbitals along the z-axis may play an essential role in O₂ adsorption for ORR.

Inspired by the computational findings, Pt₁−Ti₁−xO₂ nanosheets were experimentally fabricated, in which an electrostatic adsorption-anchorage route was employed. Initially, the monolayered Ti₁−xO₂ nanosheet host with fairly transparent characteristics was fabricated, in which the atomically dispersed titanium vacancy (Tivac) is clearly identified (Figures 2a and 2b). Whereafter, Pt²⁺ species electrostatically anchored at the Tivac sites to form Pt₁−Ti₁−xO₂. The lamellar structure with a spacing of ∼1.7 nm was detected for Pt₁−Ti₁−xO₂ nanosheets, according to the serial 0k₀ diffraction XRD peaks (Supporting Information Figure S2a). The monolayered characteristics (thickness of ∼1.1 nm) of Pt₁−Ti₁−xO₂ were further clarified (Supporting Information Figures S2b and S2c). Moreover, the Pt dopant impurity level was introduced as the electron donor, narrowing the bandgap and improving the electronic conductivity (Supporting Information Figures S2d and S2e). The Pt content was measured to be 1.27 wt % by ICP-OES. The HAADF-STEM image and energy-dispersive X-ray spectroscopy (EDS) mapped both signified the uniform distribution of mononuclear Pt within Pt₁−Ti₁−xO₂ nanosheets (Supporting Information Figure S2f). Given that, Pt loaded on a titanium oxide surface is also simulated, in which Pt locates outside the Ti lattice and coordinates with four relatively unsaturated oxygens into a PtO₄ coordination sphere.
configuration (Supporting Information Figure S3). As the high-resolution HAADF-STEM image shown in Figure 2d, the exclusive anchorage of Pt at the Ti–vacancy site was further confirmed by the integrated contrast intensity along the Ti lattice.

The XANES and EXAFS analysis were further performed to determine the refined structure of Pt1–Ti1–xO2. As shown in Ti K-edge XANES profile (Supporting Information Figure S4a), a decline of the white-line intensity of Ti in Pt1–Ti1–xO2 is distinguished, when compared with Ti1–xO2. It is mainly attributed to the charge transfer within Pt–5d and Ti–3d interaction as simulated in Figure 1d.38 With respect to the Pt L3-edge, the corresponding white-line intensity indicates that Pt stays positively charged (Figure 2e and Supporting Information Figures S4b–S4d). The Fourier transformed EXAFS (FT-EXAFS) profiles further specify the prominent peak located at ~2.0 Å exclusively from Pt–O scattering with a coordination number of 4.6 (Figure 2f and Supporting Information Figure S4e and Table S1). No other scattering contribution, especially Pt–Pt scattering at ~2.7 Å, was observed in the first-shell region, confirming the atomic dispersion of Pt1. The light-scattering path at ~3.3 Å ascribed to Pt–Ti scattering suggests the strong periodicity of Pt–O–Ti lattice. Thus, the rational designed Pt1–Ti1–xO2 is successfully fabricated (the inset in Figure 2e).

The ORR catalytic activity of Pt1–Ti1–xO2 was then evaluated in O2-saturated 0.1 M KOH with an RDE (Supporting Information Figure S5). The cyclic voltammetry (CV) curve of Pt1–Ti1–xO2 was recorded, as shown in Supporting Information Figure S6a. The significant reduction peak at ~0.86 V suggests the desired ORR catalytic activity. The ORR polarization curves obtained at various rotation rates from 400 to 2500 rpm was collected in Supporting Information Figure S6b. The electron-transfer number (n) is estimated to be ~3.88 according to the K–L equation (Supporting Information Figure S6c), indicating a dominated four-electron ORR pathway.39 Compared with the commercial Pt/C (20 wt %), Pt1–Ti1–xO2 delivers an enhanced catalytic performance (Figure 3a and Supporting Information

**Figure 3** (a) ORR LSV curves for Pt1–Ti1–xO2 and Pt/C obtained initially and after 10,000 cycles. (b) ICOHP values of Pt–d and Ti–d orbitals in Pt–O and Ti–O interactions. (c) pDOS profiles of Pt dopant, Ti, and adsorbed O for the initial O2 adsorption on Pt–Ti. (d and e) Charge density distribution (0.005 e Bohr−3) corresponding to energy windows A (d) and B (e) in (c).
Figure S6d), in terms of the more positive onset potential ($E_{\text{onset}}$) and half-wave potential ($E_{1/2}$). In addition, Pt$_1$–Ti$_{1-x}$O$_2$ exhibits a comparable $J_L$ (limiting current) with Pt/C, thus surpassing it by a factor of $>19$ in Pt mass activity (Supporting Information Figure S6e). The stability was assessed by subjecting the catalysts to continuous ORR polarization for 10,000 cycles. Notably, the superb catalytic stability of Pt$_1$–Ti$_{1-x}$O$_2$ with little change in $E_{1/2}$ was determined, while Pt/C shows a 20-mV decay in $E_{1/2}$.

The atomic dispersion of Pt$_1$ was well preserved after a 10,000-round test (Supporting Information Figure S7), in contrast to the coalescence of Pt species in Pt/C. To shed light on the excellent ORR performance of Pt$_1$–Ti$_{1-x}$O$_2$, we investigated the bonding nature for the O$_2$ adsorption on Pt$_1$–Ti$_{1-x}$O$_2$, using the side-on bonding configuration (inset in Figure 3b and Supporting Information Figure S8). As shown in Figure 3b, the $z$-axis components of Pt–5d and Ti–3d, especially $d_{z^2}$, account for $>99\%$ of total bonding for Pt–O and Ti–O interactions. Specifically, Pt/Ti–$d_{z^2}$ interacts with O$_2$–2s and 2p$_x$ orbitals to form occupied bonding levels (around $-8$ eV in Supporting Information Figures S9a and S9b), stabilizing Pt/Ti–O bond. While Ti–$d_{yz}$ and O–2p$_y$ interaction exhibits occupied bonding character near the Fermi energy, Pt–$d_{xz}$ and O–2p$_x$ interaction features antibonding states, which explains the dramatically low ICOHP value of Pt–$d_{xz}$. To provide a vivid picture of how active sites interact with O$_2$, we calculated the corresponding charge density distributions (Figures 3c–3e and Supporting Information Figures S9c–S9g). It can be clearly seen that Pt/Ti–$d_{xz}$ and O–$2p_y$ interaction exhibits bonding character, consistent with COHP analysis, while a nodal plane perpendicular for Pt–$d_{xz}$ and O–2p interaction is found, indicating the antibonding character. In general, the interaction between the $z$-axis d orbitals of the electron-rich Pt–Ti unit and oxygens dominate the O$_2$ adsorption, triggering the ORR.

In addition to intensively investigated platinum-based metals, cost-effective transition metals, especially Co and Fe, have been considered as promising candidates toward ORR. Therefore, the analogous Co$_1$–Ti$_{1-x}$O$_2$ nanosheets were fabricated and evaluated for oxygen reduction (Supporting Information Figure S10). The exclusively atomic dispersion of cobalt atom in Ti$_{1-x}$O$_2$ nanosheets were fabricated and evaluated for oxygen reduction (Supporting Information Figure S10).
could be clearly identified in the HAADF-STEM image (Supporting Information Figure S11a), without any other crystalline types of cobalt indexed. The XANES spectra specific to the Co K-edge indicates that CoO in Co-Ti₁₋ₓO₂ holds an electronic valence of approximately +2 (Supporting Information Figure S11b), as the absorption edge ranged against CoO. FT-EXAFS analysis further details the Co₁-unit (Figure 4a and Supporting Information Figure S11c and Table S2), in which the CoO₅ configuration with dominated Co-O scattering at ~1.94 Å is confirmed. In addition, the Co-Ti scattering at the long range further confirms the substitution of Co₁ at the Ti site. Thus, Co-Ti realms, given the similar configuration of the Pt-Ti unit in Pt₁₋ₓTiₓO₂, may lay a foundation for desired ORR performance.

In contrast to a negligible ORR performance of bare Ti₁₋ₓO₂ (Supporting Information Figure S12a), Co₁₋ₓTiₓO₂ delivers a desirable catalytic performance (Figure 4b), which is comparable with the Pt/C catalyst in both E₁/₂ and Jₗ. The electron-transfer number of 3.85 indicates the four-electron-transfer kinetics (Supporting Information Figures S12b-S12d). Notably, the catalytic performance of Co₁₋ₓTiₓO₂ surpasses that of Pt/C after the 10,000-cycles stability test, implying that it is a promising, cost-effective candidate for ORR.

To explain the different performance between Co₁₋ₓTi₁₋ₓO₂ and Pt₁₋ₓTi₁₋ₓO₂, we performed the orbital-resolved DOS and COHP analysis for Co₁₋ₓTi₁₋ₓO₂. In analogy to Pt₁₋ₓTi₁₋ₓO₂, the z-axis d orbitals of Co(Ti) dominate the contribution to the d-d hybridization (Figures 4c and 4d and Supporting Information Figure S13), which is quite consistent with the proposed atom-realm (AR) effect.⁷,⁷¹,⁷⁴ However, one order of magnitude smallerICOHP indicates much weaker d-d interaction in Co₁₋ₓTi₁₋ₓO₂. This is quite consistent with the XPS analysis (Supporting Information Figure S14), in which the binding energy of Ti in Pt₁₋ₓTi₁₋ₓO₂ shifts to a lower range compared with that of Co₁₋ₓTi₁₋ₓO₂, indicating the enhanced charge transfer from Pt to Ti, namely the activation of Ti. It thus may give an explanation of the inferior catalytic performance of Co₁₋ₓTi₁₋ₓO₂ compared with Pt₁₋ₓTi₁₋ₓO₂. When O₂ is adsorbed on Pt₁₋ₓTi₁₋ₓO₂/Co₁₋ₓTi₁₋ₓO₂ (referred as Pt₁₋ₓTi₁₋ₓO₂−O₂ or Co₁₋ₓTi₁₋ₓO₂−O₂) to forming Co/Pt-O and Ti-O bonds, the original d-d interaction dramatically decreases to a large extent (Supporting Information Figures S15 and S16), since the delocalized charge transfers to the absorbed oxygen. The orbital-resolved ICOHP shows that Co(Ti)−d₂ orbital dominates the d-orbital contribution to the O₂ adsorption (Supporting Information Table S3), in consistent with the crucial role of Pt(Ti)−d₂ in Pt₁₋ₓTi₁₋ₓO₂−O₂. Unexpectedly, Co-O bonding strength is similar to the Pt−O bonding strength, while the TiO−O bond in Co₁₋ₓTi₁₋ₓO₂−O₂, on the other hand, is much weaker than the Ti−O bond in Pt₁₋ₓTi₁₋ₓO₂−O₂. It is well known that the adsorbate-adsorbent bonding interaction accompanies the electron-transfer process. Therefore, we applied Bader charge analysis to estimate the electron transfer between active sites and O₂ (Figure 4d).⁴⁹ Results show that the electron transfer from Co to OCo (0.29 |e|) is similar to that from Pt to OPt (0.32 |e|), with the catalyst changed from Co₁₋ₓTi₁₋ₓO₂ to Pt₁₋ₓTi₁₋ₓO₂. However, the electron transfer from Ti to OTi increases significantly (from 0.33 to 0.45 |e|), coinciding with the COHP analysis. Such interesting findings imply that the inferior catalytic performance of Co₁₋ₓTi₁₋ₓO₂ compared with Pt₁₋ₓTi₁₋ₓO₂ may be attributed to the substantial activation of Ti atom via d-d hybridization by doping Ti₁₋ₓO₂ from Co to Pt. Therefore, the orbital-level insights unraveled in this work demonstrate that the orbital-level, and even spin-level, regulation in catalysts is crucial for the precise catalysis. Given the catalytic descriptors (charge, orbital, spin, etc.), this work thus introduces the AR catalysis, exactly as the quantum catalysis (QC) does, to fill the gap between single-atom catalysis and electronic catalysis.ⁱ²,⁵⁰ Therefore, engineering AR catalysts, especially the orbital catalysts and spin catalysts, could be an effective strategy toward highly efficient and precise catalysis.

Conclusion
We applied a new strategy to investigate the role of d orbitals in ORR catalyzed by Pt₁₋ₓTi₁₋ₓO₂. The orbital-resolved bonding analysis based on DFT calculations indicate that the z-axis d orbitals of dopants/Ti make the dominant contribution to the d-d hybridization. Moreover, further analysis clarifies that the z-axis d orbitals of the catalytic unit also play a crucial role in O₂ adsorption. The dopants serve a dual function, not only as an active center for ORR but also as a trigger of the catalytic activity of the neighboring Ti. In light of the d-orbital analysis, Pt₁₋ₓTi₁₋ₓO₂ and Co₁₋ₓTi₁₋ₓO₂ were fabricated, and the ORR performance measurements show a superior catalytic activity of Pt₁₋ₓTi₁₋ₓO₂ compared with Co₁₋ₓTi₁₋ₓO₂. The orbital-resolved strategy present in this work offers a valuable tool to uncover the role of d orbitals of active centers in catalytic reactions so as to guide rational catalyst design via the precise regulation of the d orbitals of catalysts.

Supporting Information
Supporting information is available and contains supplementary characterization and computational data, including XRD patterns; SEM, AFM, and STEM images; XPS and XAFS spectra; electrochemical CV and LSV curves; and DOS and COHP analyses.

Conflict of Interest
The authors declare no conflict interest.
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