

Single-Atom Photocatalysts on TiO₂ : Insights from X-ray Absorption Spectroscopy

Yingying Li^a, David Morris^b, Peng Zhang^{*b}

^a State Key Laboratory of Integrated Optoelectronics, Key Laboratory of UV Light-Emitting Materials and Technology of Ministry of Education, School of Physics, Northeast Normal University, Changchun, 130024, China.

^b Department of Chemistry, Dalhousie University, Halifax, NS, Canada.

Corresponding Author: peng.zhang@dal.ca

Abstract

Surface modification of TiO₂ with single-atom catalysts (SACs) is an effective strategy for enhancing photocatalytic efficiency. However, thorough characterization of SACs at the atomic scale remains challenging. X-ray absorption spectroscopy (XAS) offers unique advantages for the in-depth analysis of TiO₂-supported SACs. By employing XAS, the local atomic structure, oxidation state, and electronic properties of the SACs, as well as the underlying photocatalytic mechanism, can be revealed. Herein, we present a short review on the application of XAS in studying TiO₂-supported SACs. We first elucidate the key role of XAS in simultaneously probing the structure and electronic properties of monometallic SACs across different periods. Next, we discuss XAS studies of bimetallic SACs

from the perspective of each constituent element and highlight the element-specific capabilities of XAS for analyzing multi-element SACs. Finally, we demonstrate how *in situ* XAS can effectively monitor structural and electronic property changes in SACs under real photocatalytic reaction conditions. Overall, this review highlights the unique advantages of XAS in achieving a more comprehensive understanding of the structure–property relationships in SACs, ultimately aiding the rational design of future photocatalysts. Additionally, we provide practical suggestions for utilizing XAS more efficiently in the analysis of various SAC systems.

Keywords: X-ray absorption spectroscopy, single-atom photocatalysts, TiO₂ support, local structure, electronic properties, *in-situ* spectroscopy

1. Introduction

TiO₂, a typical semiconductor material, has been widely used in photocatalysis and remains a subject of ongoing research.^[1] To further improve its photocatalytic efficiency, various surface modification strategies have been proposed,^[2] including heterojunction construction and cocatalyst modification.^[3] Among these, single-atom catalyst (SAC) modified TiO₂ exhibits excellent photocatalytic performance.^[4] SACs maximize atomic utilization and significantly enhance catalytic activity

and selectivity through unique interfacial interactions with the TiO_2 support.^[5] Compared to nanoparticles, SACs composed of elements such as Pt, Au, Pd, Rh, and Cu demonstrate superior photocatalytic activity when atomically dispersed.^[6] However, fully elucidating their atomic-scale structure and electronic properties remains a significant challenge.

X-ray absorption spectroscopy (XAS) has emerged as a powerful technique to analyze the atomic structure and electronic properties of SACs.^[6d,7] Traditionally, high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) is used to provide atomic-scale structural information on SACs, while X-ray photoelectron spectroscopy (XPS) is used to reveal their electronic properties.^[8] XAS allows for both atomic-scale structural information and electronic properties to be analyzed using one technique, making it a critical tool in SAC research due to its element specificity, high sensitivity, and applicability under diverse support and reaction conditions.^[9] Specifically, X-ray absorption near-edge structure (XANES) primarily elucidates electronic properties and charge transfer mechanisms in catalytic processes, while extended X-ray absorption fine structure (EXAFS) provides detailed atomic structural information.^[10] These two spectral regions are complementary, for instance, changes in the Ti-O coordination number (CN) observed in EXAFS often correlate with variations in the Ti oxidation state or electronic structure detected in the

XANES region.^[11]

For TiO₂-supported SACs, XAS provides crucial information, including oxidation states, d-electron density, CNs, and bond distances.^[12] Notably, for transition metals, XAS serves as an integrated technique for characterizing both electronic and structural properties.^[13] Additionally, it can identify light atoms such as O and Cl in the coordination environment.^[14] For metals with similar atomic numbers, which are difficult to resolve using imaging techniques, XAS is capable of distinguishing them based on their distinct absorption edge energies.^[15] Furthermore, XAS can be performed under atmospheric pressure in air, as high-energy X-rays exhibit strong penetration ability and are not significantly absorbed by reaction gases or air.^[16] By adjusting the test temperature and atmosphere, changes in the electronic and structural properties of metal SACs can be monitored in real time, revealing the dynamic evolution of photocatalytic activity.^[17]

Herein, we present a short review on the application of XAS in the analysis of TiO₂-supported SACs. First, we summarize the advantages of XAS for characterizing both monometallic and bimetallic SACs. Subsequently, we highlight the critical role of *in situ* XAS in studying photocatalytic reactions. This review aims to provide critical perspectives and practical guidance for the XAS analysis of TiO₂-supported SACs, with the goal of advancing the understanding of their photocatalytic

mechanisms and enabling the rational design of future photocatalysts.

2. XAS of TiO₂-supported monometallic SACs

2.1 5d-transition metal SACs

For 5d-transition metals, imaging techniques such as HAADF-STEM have been utilized to achieve atomic-scale structural analysis.^[18] However, these techniques are inherently limited in their ability to provide electronic information.^[19] XAS has emerged as an integrated analytical technique capable of simultaneously characterizing both electronic and structural properties. Specifically, the L₃-edge excitation corresponding to the $2p_{3/2}$ to $5d$ transition under X-ray irradiation provides valuable information about the electronic properties.^[20] XANES reveals the oxidation states of metals by probing d-electron density, which can help identify the optimal valence state for catalytic activity.^[21] EXAFS analysis provides detailed atomic-scale structural information, enabling the probing of interactions at the metal-TiO₂ interface.^[22] These insights are crucial for exploring catalytic mechanisms and guiding the development of high-performance photocatalysts.

Chen et al. successfully assembled single Pt atoms on a defective TiO₂ support for photocatalytic hydrogen production.^[23] From the XANES spectra of the Pt L₃-edge (Figure 1a), the white-line intensity of Pt₁/TiO₂ falls between that of Pt foil and PtO₂, indicating charge transfer between

single Pt atoms and surrounding oxygen atoms, arising from enhanced metal–support interactions. FT-EXAFS analysis (Figure 1b-1d) confirmed the isolated nature of the single Pt atoms. Based on the CN and bond distances derived from EXAFS fitting, an atomic model was constructed with the aid of density functional theory (DFT) calculations. The valence states of O and Ti were further examined by XPS, supporting the interpretation of the electronic state of the SACs.

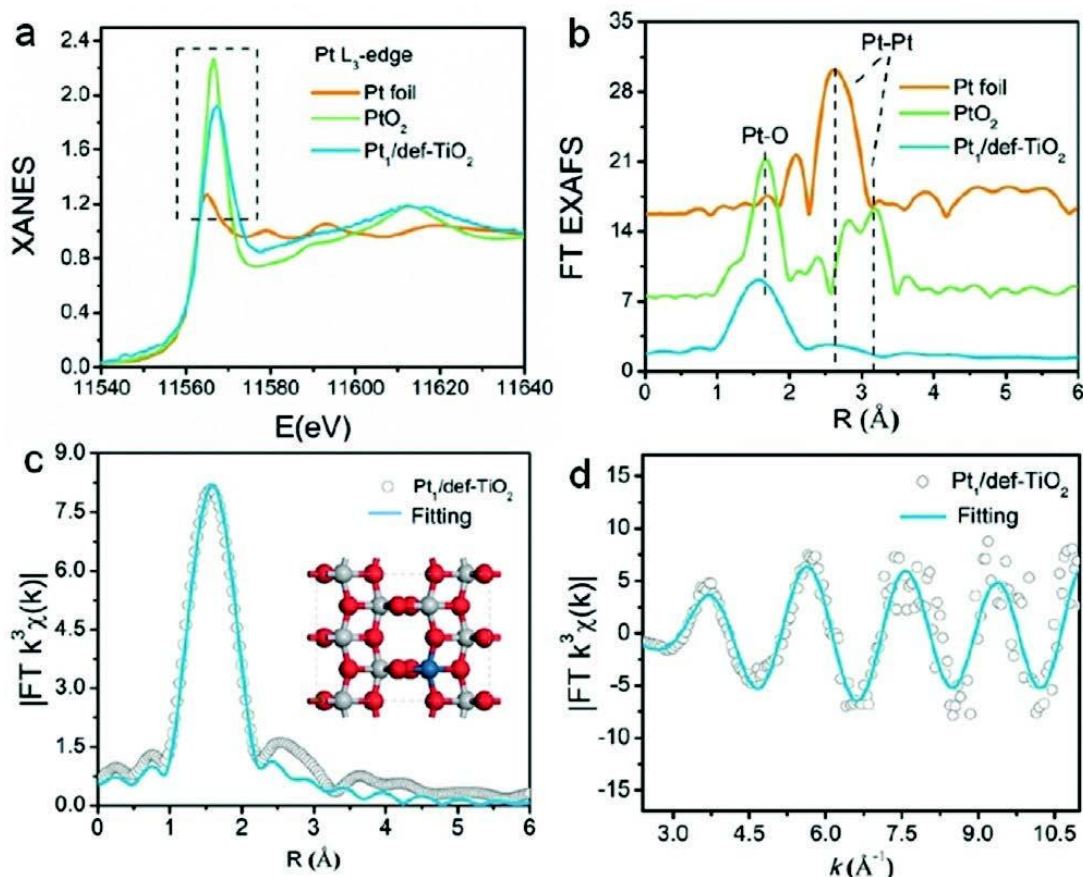


Figure 1: (a) XANES spectra of the Pt $L_{3\text{-edge}}$ for the Pt_1/TiO_2 catalyst, Pt foil, and PtO_2 ; (b) Fourier-transformed (FT) EXAFS spectra of Pt_1/TiO_2 catalyst, Pt foil, and PtO_2 . (c) EXAFS R-space fitting curve (blue line) and experimental data (circles) for the Pt_1/TiO_2 catalyst. (d) EXAFS k-space fitting curve (blue line) and the experimental data (circles) for the Pt_1/TiO_2 catalyst.^[23]

Feng et al. reported the uniform dispersion of single tungsten atoms

on the surface of TiO_2 nanoparticles, forming isolated active sites and thereby significantly enhancing CO_2 reduction efficiency.^[24] It is worth noting that distinguishing W and Ti atoms based on their brightness in HAADF-STEM is particularly challenging, as shown in Figure 2a. XAS provided the most direct evidence confirming the existence of single W atoms in this work (Figure 2b), underscoring its unique advantages over imaging techniques for atomic-scale structural characterization. Similar studies have also used XAS to probe the atomic structures of W-doped TiO_2 , due to the large difference in their absorption-edge energies.^[25] Collectively, these findings highlight the indispensable role of XAS in elucidating the structural and electronic properties of SACs.

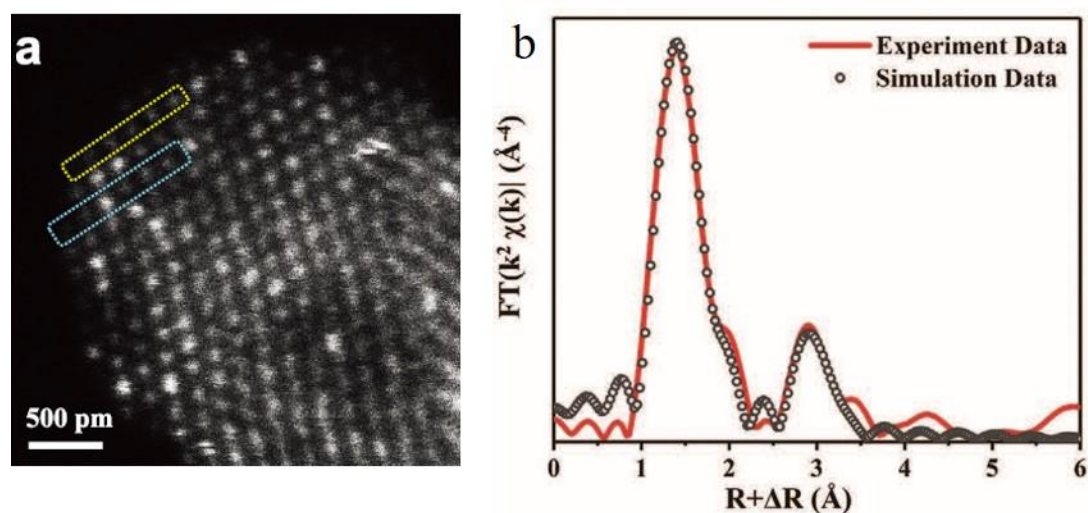


Figure 2: (a) HAADF-STEM image of W_1/TiO_2 . (b) Comparison of the FT-EXAFS spectra between the experimental data and the fitted results for W_1/TiO_2 .^[24]

Overall, for TiO_2 structures modified with heavy single atoms, it is necessary to combine HAADF and EXAFS to resolve the structure of SACs on the TiO_2 surface. To elucidate the electronic properties, XANES

and XPS are valuable analytical tools.^[26] XAS can simultaneously provide electronic and structural information, making it a powerful technique for the comprehensive characterization of such catalytic systems.

2.2 4d-transition metal SACs

HAADF-STEM has been employed for imaging heavier metal elements at the atomic scale.^[27] However, this technique is limited in its ability to resolve light elements surrounding metal atoms, which play a critical role in photocatalytic activity.^[28] In contrast, XAS provides crucial insights into atomic structure, particularly the chemical bonds between metal atoms and light elements such as Cl and O.^[29]

Liu et al. designed an atomically dispersed palladium–titanium oxide catalyst (Pd_1/TiO_2) with a Pd content of up to 1.5%, which showed high catalytic activity for C=C bond hydrogenation, achieving nine-fold higher performance than commercial Pd catalysts.^[14] EXAFS analysis revealed that only Pd-O bonds were observed at 1-2 Å range, with no Pd-Pd bond peak, as shown in Figure 3a. Notably, the reaction rate of Pd_1/TiO_2 was maintained after 20 cycles, whereas that of unsupported H_2PdCl_4 decreased after the second cycle. They found that the presence of Pd-Cl bonds (Figure 3b) hindered catalysis, highlighting the crucial role of light-element coordination around metal atoms in directly affecting catalytic activity. XAS plays a key role in distinguishing these light elements, a task

unachievable through imaging techniques alone.

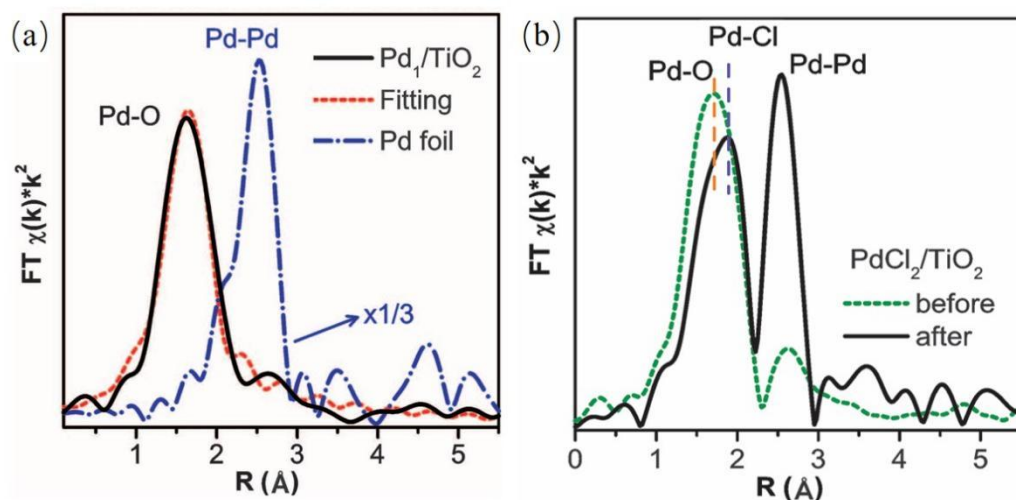


Figure 3: (a) FT-EXAFS spectra of Pd₁/TiO₂ and bulk Pd foil at the Pd K-edge, showing the coordination environment of Pd atoms; (b) FT-EXAFS spectra at the Pd K-edge of PdCl₂/TiO₂ before and after the catalytic reaction.^[14]

Guo et al. employed XANES to analyze the electronic structure and oxidation state of Pd in Pd/TiO₂ catalysts.^[30] By comparing the spectra with PdO and Pd foil references, they confirmed that the Pd SACs exhibited a positive valence state, consistent with the XPS results. In this study, XANES was used not only for structural characterization but also to reveal the catalytic reaction mechanism, thereby aiding performance optimization.

For 4d transition metals, research often focuses on K-edge analysis, which corresponds to the 1s to 4p electronic transition.^[31] However, the role of d-electrons is more important in catalytic processes.^[32] The L-edge absorption (2p → 4d) in the XAS spectrum is therefore more valuable for revealing catalytic mechanisms.^[33] By combining K-edge and L-edge information, a more comprehensive understanding of the electronic

properties of 4d transition-metal SACs can be achieved.^[34] However, the relatively low absorption energies of the L-edge necessitate the use of soft X-ray.^[35] When designing soft X-ray absorption spectroscopy experiments, it is essential to identify and select a synchrotron beamline that covers the required photon energy range of the absorption edge. Representative soft X-ray beamlines are listed in Table 1.

Table 1: Representative soft X-ray beamlines at synchrotron light sources.

Light Source	Beamline	Energy Range
Shanghai Synchrotron Radiation Facility (SSRF)	BL14W1	4.5-50KeV
High Energy Photon Source (HEPS)	ID46	4.8-45keV
Beijing Synchrotron Radiation Facility (BSRF)	1W1B	4.8-22.8keV
Beijing Synchrotron Radiation Facility (BSRF)	4B7B	50eV-1700eV (XANES)
Canadian Light Source (CLS)	SXRMB	1.7-10 KeV
Advanced Photon Source (APS)	9-BM	2.1-40 KeV
The European Synchrotron (ESRF-EBS)	ID03	11.0-60.0 KeV
MAX IV	FlexPES	43 – 1550 eV
Spring-8	BL27SU	2.1-3.3 KeV

2.3 3d-transition metal SACs

For TiO₂-supported metals, 3d transition metals such as Cu, Fe, Co and Ni, which are in the same period as Ti, are considered promising

alternatives to noble metals due to their variable valence and cost-effectiveness.^[36] However, for elements within the same period, it is challenging to distinguish them using image techniques. XAS overcomes this limitation due to the unique absorption edges of each element. For example, it is difficult to distinguish between Cu and Ti in HAADF-STEM images, as shown in Figure 4a. However, the Cu K-edge is ~8979 eV, whereas the Ti K-edge is ~4966 eV.^[37] This pronounced energy difference allows these two elements to be clearly distinguished by XAS.

Fang et al. employed EXAFS to investigate the coordination environment of Cu on TiO₂-supported catalysts, as shown in Figure 4b.^[38] For Cu₁/TiO₂ SACs, the main EXAFS peak corresponded to the Cu-O interatomic distance, while the second shell indicated Cu-Ti interactions, confirming the formation of a Ti-O-Cu structure. For CuO_x/TiO₂ nanoparticles, EXAFS analysis suggested coexistence of CuO and Cu₂O species. XANES elucidated the oxidation state and coordination environment of isolated Cu atoms, as shown in Figure 4c. In Cu₁/TiO₂ SACs, the pre-edge features of the Cu XANES aligned with those of the Cu₂O reference, indicating that the Cu single atoms primarily exist in the Cu⁺¹ oxidation state.

In many cases, a variety of characterization techniques are used to identify the valence state of 3d SACs.^[39] For example, Shen et al. confirmed that the valence state of Cu was between +1 and +2 through

XANES.^[40] The intermediate valence state was further confirmed by Cu LMM Auger electron spectra, XPS analysis and theoretical calculations. This approach underscores the importance of using multiple complimentary techniques for accurate electronic structure determination.

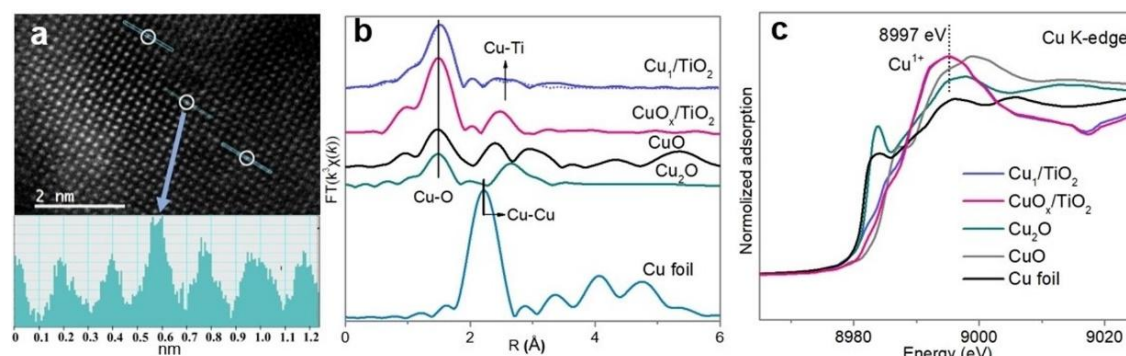


Figure 4: (a) HAADF-STEM image of Cu₁/TiO₂ SACs; (b) Normalized FT-EXAFS spectra of the Cu K-edge for Cu₁/TiO₂ and CuO_x/TiO₂ catalysts; (c) XANES spectra of the Cu K-edge for Cu₁/TiO₂ SAC and CuO_x/TiO₂ catalyst.^[38]

3. XAS of TiO₂ supported bi-metallic SACs

3.1 Bi-metallic elements from different periods

XAS is particularly powerful for analyzing the electronic and structural information of individual elements in multi-metallic systems. By combining XANES and EXAFS data, detailed information on each constituent element can be obtained. Furthermore, by integrating the unique spectral features of each element, more detailed structural and electronic information on the bimetallic system can be obtained. The datasets from the two elements in bimetallic SACs complement and corroborate each other, providing a comprehensive picture of the system.

Bimetallic SACs composed of Cu and Au have been widely employed

in the photocatalytic reduction of CO_2 to C_2H_4 . However, the detailed photocatalytic mechanism remains ambiguous. To obtain an improved understanding, Xie et al. studied the aggregation and deactivation of CO intermediates during Cu SAC photocatalytic CO_2 reduction using HAADF-STEM and XAS. [41] They also successfully synthesized Cu_5Au_1 on the surface of TiO_2 with isolated Au atoms embedded in the Cu lattice. [42] The existence of Cu-Au bonds was further confirmed by XANES and EXAFS analysis, as shown in Figure 5. Notably, the Au white-line peak in the XANES spectra is relatively weak and insensitive in conventional XAS measurements. To enhance the sensitivity of the Au white-line analysis, we suggest that high-energy resolution fluorescence-detected X-ray absorption spectroscopy (HERFD-XAS) should be employed in future studies. [43]

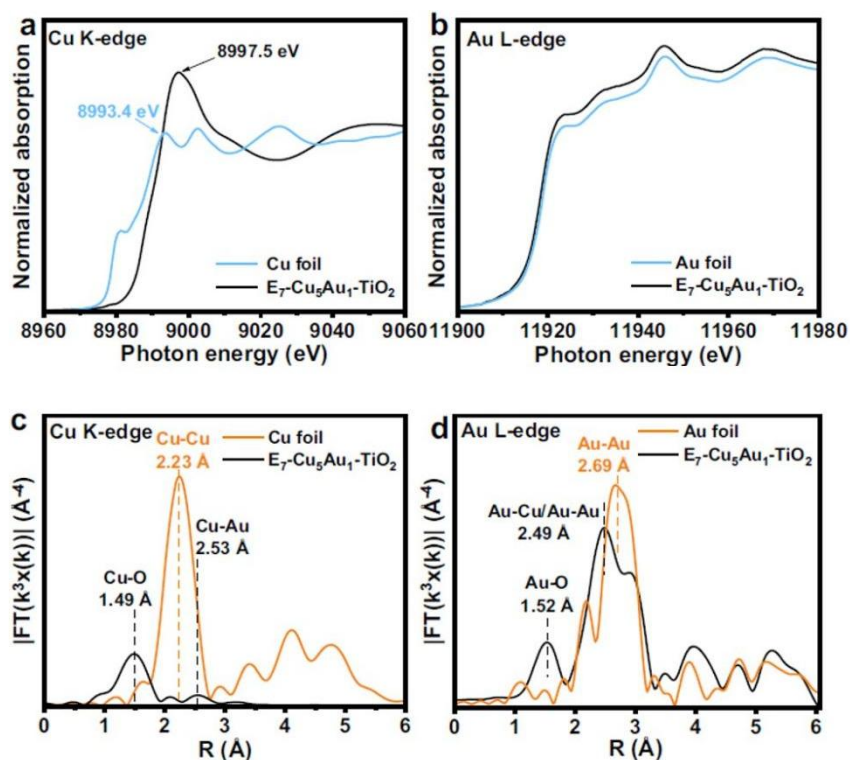


Figure 5: XANES analysis of $\text{Cu}_5\text{Au}_1\text{-TiO}_2$ and reference samples at the (a) Cu K-edge and (b) Au L_3 -edge. Corresponding K_3 -weighted FT-EXAFS spectra for $\text{Cu}_5\text{Au}_1\text{-TiO}_2$ and references at the (c) Cu K-edge and (d) Au L_3 -edge.^[42]

3.2 Bimetallic elements from the same period

For bimetallic SACs consisting of two elements with similar atomic numbers, it is challenging to use conventional structural analysis techniques, such as TEM, to distinguish between the two elements. XAS overcomes this challenge due to its element specific capability. Therefore, it can offer more comprehensive information on the structure and electronic properties of bimetallic SACs from the perspective of each element.

Tang et al. synthesized RuMo/TiO_2 bimetallic SACs and conducted a comprehensive XAS analysis to elucidate the structural and electronic properties.^[44] The spectra (Figure 6a) and fitting results showed that the valence state of Ru in $\text{Ru}_4\text{Mo}_1/\text{TiO}_2$ and Ru_6/TiO_2 ranged from 0 to +4. Due to electronic interactions, the presence of Mo atoms in $\text{Ru}_4\text{Mo}_1/\text{TiO}_2$ caused the Ru atoms to exhibit a higher valence electron density compared to Ru_6/TiO_2 . As the Mo:Ru ratio increased, a significant shift of the Ru absorption edge to higher energy was observed, indicating an increase in the oxidation state of Ru. Conversely, the valence state of Mo in $\text{Ru}_4\text{Mo}_1/\text{TiO}_2$ decreased, corresponding to the increase in the Ru valence state, as shown in Figure 6b. This finding supports a strong electronic interaction between Ru and Mo atoms. EXAFS analysis revealed a single

peak at ~ 1.5 Å in $\text{Ru}_4\text{Mo}_1/\text{TiO}_2$, corresponding to the first shell Ru-O path, as shown in Figure 6c. Similarly, only a single peak at ~ 1.3 Å attributed to the Mo-O path was observed, as shown in Figure 6d, confirming the atomic dispersion of Mo. These results provide valuable insights into the structural and electronic properties of the RuMo/TiO_2 system, highlighting the significant role of XAS in SAC characterization.

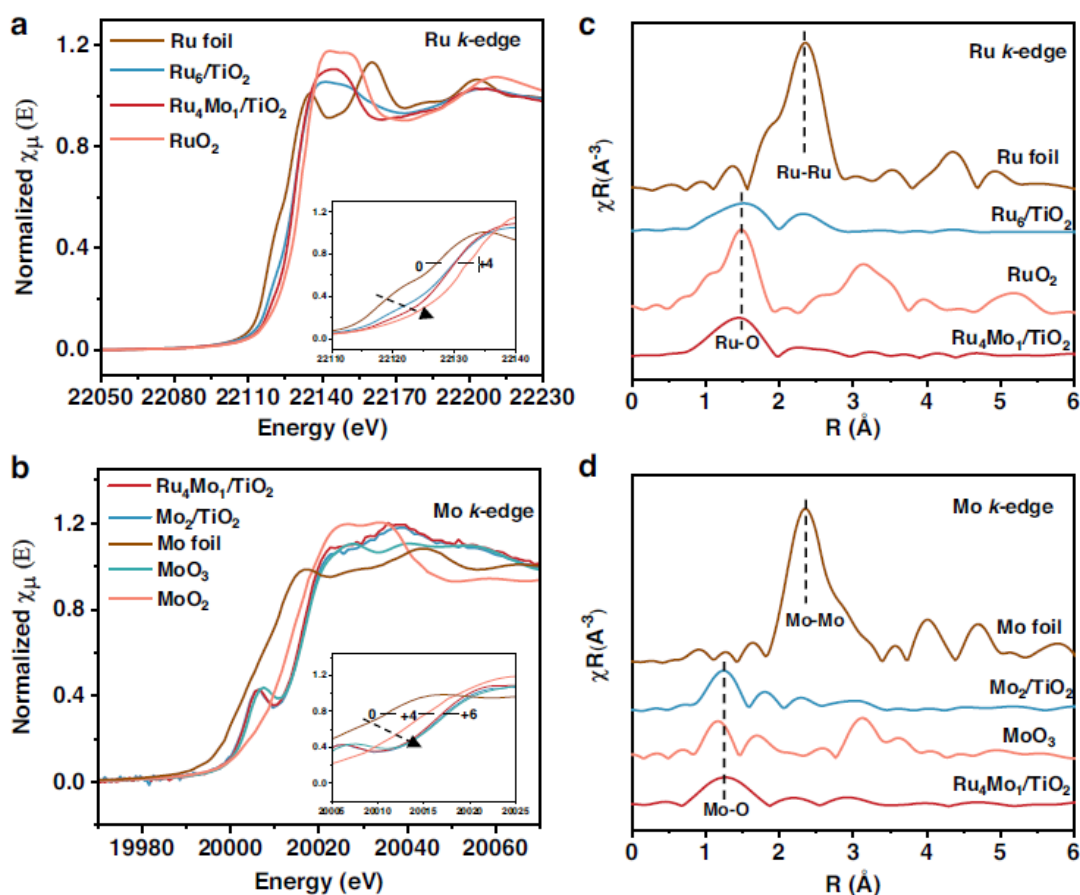


Figure 6: Structural characterization by XAS. Normalized XANES spectra at the (a) Ru K-edge (inset: absorption edge positions of Ru) and (b) Mo K-edge, (inset: absorption edge positions of Mo). FT-EXAFS spectra of (c) Ru-containing samples and (d) Mo-containing samples.^[44]

Wei et al. successfully prepared Pt-Au dual-atom catalysts through a two-step deposition–precipitation method.^[45] The Pt-Au dual-atom

photocatalyst exhibited superior photocatalytic hydrogen production performance compared to monoatomic Pt and Au catalysts. Numerous bright spots were observed in HAADF-STEM images, confirming the distribution of atomically dispersed Au and Pt atoms, as shown in Figures 7a and 7b. However, distinguishing between the two elements is difficult due to their similar atomic numbers. XAS provided element-specific information, revealing the coordination environments of Pt and Au atoms and offering key insights into the active sites of the catalysts. The atomic dispersion and oxidation states were further analyzed by FT-EXAFS spectra (Figures 7c and 7d). These results were consistent with the findings from XPS and HAADF-STEM, enhancing the reliability and comprehensiveness of the structural characterization.

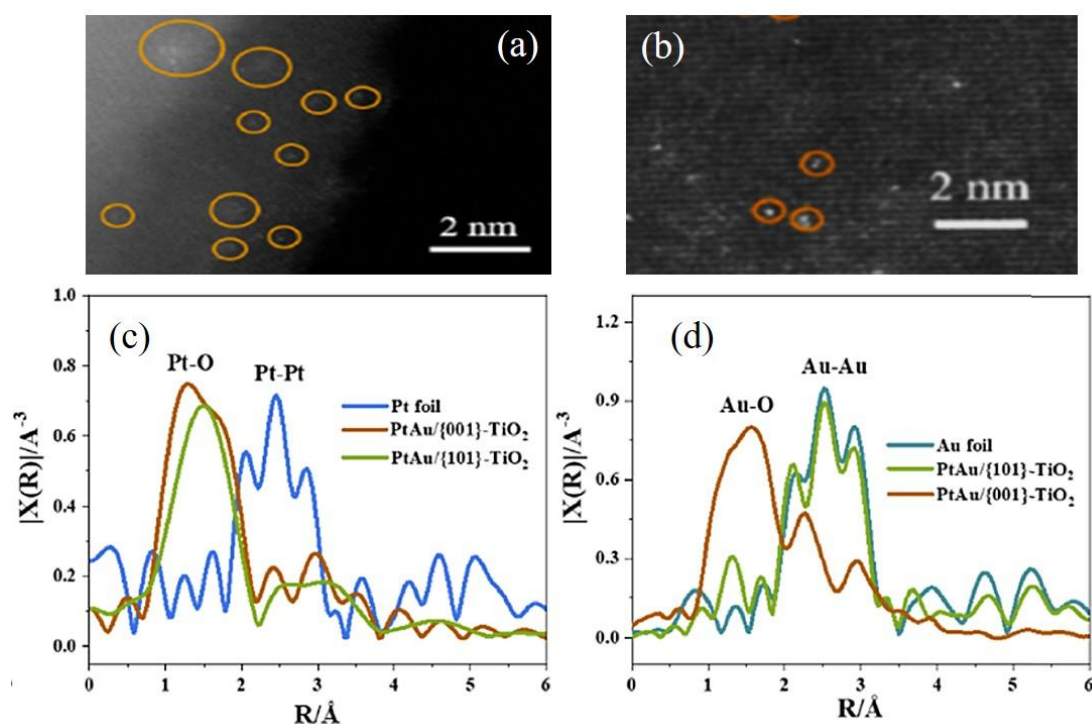


Figure 7: HAADF-STEM images of (a) PtAu/{001}-TiO₂ and (b) PtAu/{101}-TiO₂. FT-EXAFS spectra of the (c) Pt L₃-edge and (d) Au L₃-edge.^[45]

As Figure 7 shows, when two metals are in the same period, it is difficult to distinguish them at atomic resolution by HAADF-STEM. XAS however remains a robust technique for accurately identifying different metal atoms. The quality of EXAFS analysis depends strongly on the relative positions of the elements in the periodic table. For example, Ru-Mo systems exhibit excellent EXAFS fitting, whereas Pt-Au systems do not. For 4d transition metals, K-edge analysis is typically employed. The K-edge absorption energy difference between Ru and Mo is ~ 2700 eV, while the L_3 -edge difference between Pt and Au is only ~ 360 eV, which is too small to clearly distinguish the two elements. For 5d transition metals, the L_1 -edge offers higher energy and greater separation of absorption edges for elements with similar atomic numbers. For example, the difference in L_1 -edge absorption energy is much higher than that of the L_3 -edge. Therefore, L_1 -edge analysis is suggested for Au-Pt SACs to improve structural resolution.

4. *In situ* XAS under real conditions

Employing *in situ* techniques enables the real-time monitoring of changes in the surface structure and electronic states of catalysts under real reaction conditions. At present, *quasi-in situ* XPS and *in situ* TEM are predominantly adopted in *in situ* catalytic research. In comparison, *in situ* XAS possesses two distinct advantages. Firstly, XPS and TEM are

typically conducted under vacuum or at least low-pressure conditions. This makes them unsuitable for monitoring photocatalytic reactions at ambient pressure and imposes stringent requirements on reactor design. In contrast, XAS can be performed at ambient pressure, enabling monitoring of photocatalytic reactions under realistic conditions. Secondly, XAS employs high-energy X-rays, which can penetrate the sample cell, making it particularly effective for measurements in liquid-phase or mixed-phase environments. This capability enables real-time tracking of interactions between catalysts and adsorbed reactants during photocatalytic processes, which is crucial for gaining a more complete understanding photocatalytic mechanism.

To better understand catalytic kinetics, Tesvara et al. explored the mechanism of CO oxidation on highly dispersed Pt SACs supported on TiO_2 using *in situ* XAS at the Pt L_3 -edge.^[46] By comparing the white-line intensity before and after exposure to CO at 160°C, the oxidation state of the SACs was revealed. Zhou et al. studied ligand-modified Pt SACs supported on TiO_2 (Figure 8).^[47] *In situ* XAS was performed at different temperatures and under various atmospheres, demonstrating that the activity and stability of the catalysts depended on the choice of ligand and the coordination environment of Pt atoms. Lu et al. reported thermally stable Pd SACs supported on TiO_2 .^[48] The local coordination environment of Pd atoms was monitored in real time by *in situ* XAS under varying

atmospheres and temperatures. EXAFS analysis revealed that H₂-treated Pd single atoms exhibited decreased Pd-O coordination while forming short Pd-Ti bonds, which stabilized the Pd single atoms. During CO oxidation, Pd-Ti coordination was partially replaced by Pd-O. This unique Pd coordination environment enhanced CO adsorption and activating surrounding oxygen species. This unique coordination environment enabled both Mars–van Krevelen and Eley–Rideal pathways, resulting in excellent catalytic performance. Overall, *in situ* XAS directly revealed the structural evolution of single-atom sites under different reaction conditions, linking these transformations to kinetic parameters and reaction pathways.

Taken together, these representative studies demonstrate that *in situ* XAS provides detailed, real-time insights into the structural and electronic evolution of SAC photocatalysts. This capability enhances our understanding of photocatalytic mechanisms and guides the rational design of high-performance catalytic systems.

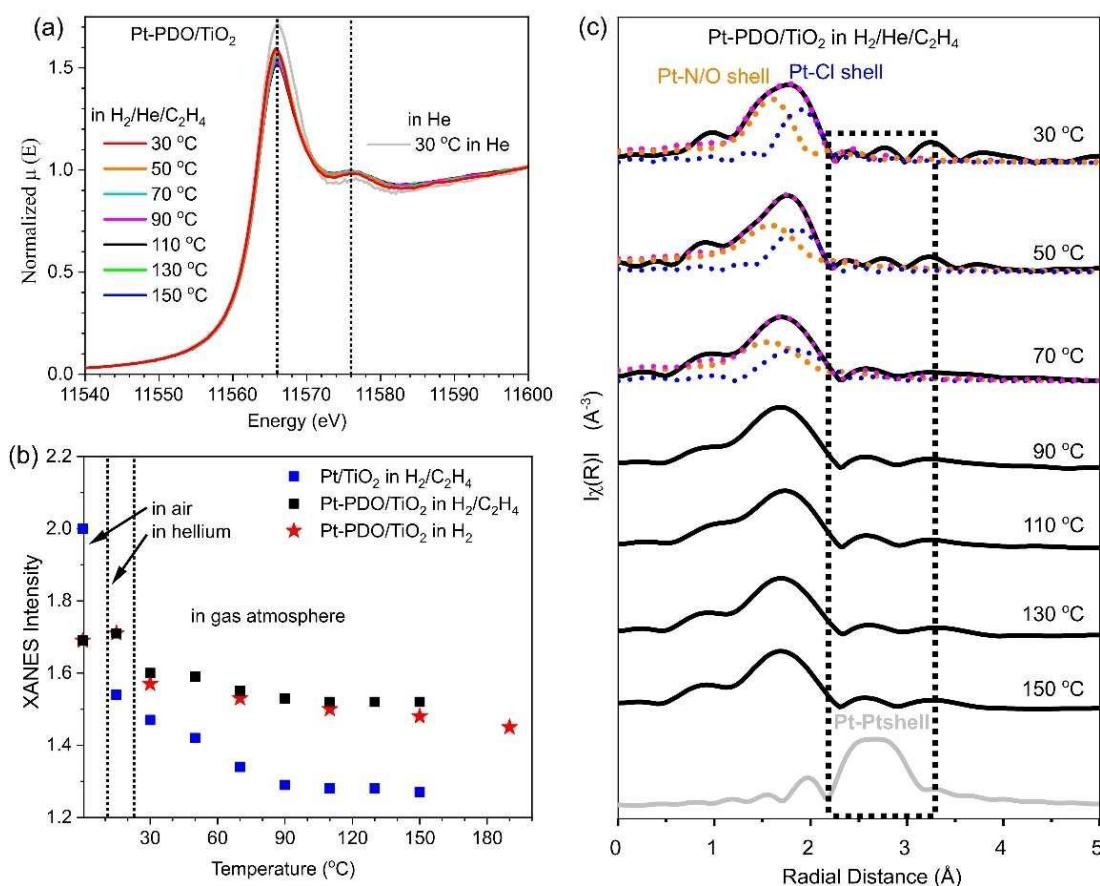


Figure 8: (a) Pt L₃-edge XANES spectra of Pt/TiO₂ under reaction conditions from 30 to 150°C. (b) XANES white-line intensity for Pt in reaction gas (blue, black) and in H₂ (red) at different temperatures. Data points recorded at room temperature in air and at 30°C in helium are shown at the left. (c) Fourier-transformed magnitude of k^2 -weighted EXAFS spectra of Pt/TiO₂ under reaction conditions from 30 to 150°C, with fittings for the first three spectra.^[47]

5. Conclusion and Outlook

In summary, we have discussed the unique advantages of XAS in characterizing TiO₂-supported SACs. For monometallic SACs, XAS provides atomic-scale insights, simultaneously yielding both electronic and structural information. Specifically, XAS analysis elucidates the coordination environment (particularly light-element coordination around metal centers), the oxidation state of metal atoms, and charge transfer

mechanisms between SACs and TiO_2 . For bimetallic SACs, XAS enables element-specific analysis of both electronic and structural properties, providing a comprehensive understanding of the catalysts. By selecting the unique absorption edges of target metals, XAS efficiently distinguishes and identifies metal atoms with similar atomic numbers.

The utilization of high-energy X-rays and the ability to operate without vacuum conditions make XAS particularly advantageous for *in situ* characterization of photocatalytic reactions. It facilitates real-time monitoring of structural evolution under dynamic reaction conditions, including variations in temperature, atmosphere, and liquid-phase environments. This capability overcomes limitations of conventional techniques such as XPS and TEM, providing critical insights into structure–property relationships and valuable guidance for the rational design of high-performance photocatalysts.

Despite these advancements, continued development of XAS is still required. For instance, XANES simulations and EXAFS fitting approaches require further refinement to yield more accurate and detailed information. Additionally, integrating experimental XAS with computational methods such as DFT and machine learning could further enhance its analytical power for studying complex catalytic systems. The application of *in situ* XAS could also be advanced through the design of improved reaction cells and more sensitive X-ray detection equipment.

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