HIGHLIGHT

Tracking dynamic evolution of catalytic active sites in photocatalytic CO$_2$ reduction by in situ time-resolved spectroscopy

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In situ time-resolved spectroscopy is an effective method to monitor the catalysis reaction in real time and reveal the catalytic mechanistic pathway. The dynamic evolution of coordination and electronic structures of catalytic active sites during the CO$_2$ reduction reaction is still a "black box," impeding the design of high-efficiency catalysts. In a recent report published in *J. Am. Chem. Soc.*, by multiple in situ time-resolved spectroscopy, Xiong and co-workers successfully detected the dynamic evolution and photoinduced charge transfer process of terpyridine nickel(II) complex catalysts in photocatalytic CO$_2$ reduction reactions.

The rapid development of society requires more and more energy supply. At this stage, the supply of energy mainly depends on fossil energy. Excessive emissions of CO$_2$ caused by the burning of fossil energy cause serious environmental problems. In addition, the non-renewability and shortage of fossil energy bring about an energy crisis. In this case, photocatalytic CO$_2$ reduction is of great significance. It can directly use endless solar energy to convert CO$_2$ into hydrocarbon fuel, so it is considered as an effective way to achieve the carbon cycle [1–8]. Homogenous photocatalysts with enzyme-like properties can be an ideal candidate to drive the artificial photosynthesis due to its high selectivity and activity [9]. In homogenous catalyst systems, the catalytic activity can be adjusted by the coordination number and the ligand type around the metal ion. To better understand the reaction mechanism and optimize the performance of catalysts, great efforts have been made to use ex situ spectral testing instruments to predict the reaction mechanism of photocatalytic

reaction process [10–12]. However, the ex situ characterizations cannot achieve real-time monitoring reaction pathways due to the dynamic reaction system. Thus, the reaction mechanism of photocatalytic reaction process is still incomplete, which greatly prevented the further optimization of the catalyst design [13–15]. In addition, the reaction pathways were largely depended on the dynamic evolution of coordination and electronic structures of catalysts during photocatalytic CO$_2$ reduction. Thus, it was necessary to use operando, time-resolved and element-specific spectroscopic techniques to trace the reaction pathway and obtain key information about how homogeneous catalysts work effectively in the reaction process [16].

In a recent report published by *J. Am. Chem. Soc.*, Xiong and co-workers at Hefei National Laboratory for Physical Sciences at the Microscale in China used terpyridine nickel(II) ([Ni(tpy)$_2$]c^{2+}) complex as a catalyst model to track the mechanistic pathway of photocatalytic CO$_2$ reduction by employing the time-resolved X-ray absorption spectroscopy (TR-XAS), other spectroscopic techniques and theoretical computation [17]. The authors firstly proposed the use of in situ spectroscopy to track the change of the intermediate product [Ni(tpy)$_2$]$^{2+}$. Based on the obtained data of dynamic coordination and electronic structure, the action of catalyst, photosensitizers, electron donors and solvents was further elaborated in photocatalytic CO$_2$ reduction.

TR-XAS technology has very good atomic selectivity [18]. It can effectively avoid Ru photosensitizers or 1,3-dimethyl-2-phenyl-2,3-dihydro-1Hbenzo[d]imidazole (BIH) organic solvents in the study of complex CO$_2$ reduction processes. The operando TR-XAS technology is creatively employed and focused on the dynamic coordination and electronic structures of Ni sites during the reaction. Figure 1a shows the schematic illustration of operando TR-

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XAS technology. The obtained extended X-ray absorption fine structure (EXAFS) data shown in Fig. 1b, d mainly include two kinds of spectral information: From the ground-state spectrum and the experimental transient spectrum after photoexcitation, the information of the Ni intermediate can be obtained by removing the environmental impact data in the experimental transient spectrum. By analyzing the information of the Ni intermediate, it is found that the near-side position shifted to the left and the white line peak position decreased, both of which proved that the

coordination environment of nickel has changed greatly. Accordingly, the geometry of the Ni catalyst has changed from a six-coordinated Ni-N$_6$ octahedral structure (Fig. 1c) to a penta-coordinated distorted tetrahedron configuration (Fig. 1e), the appearance of coordination changes indicates the presence of a Ni (I) intermediate, and the change of the bond length between the central Ni and the surrounding ligand can also prove the existence of Ni (I) intermediate. Based on the data before and after illumination, it is obvious that a terpyridine ligand was isolated from the excited Ni
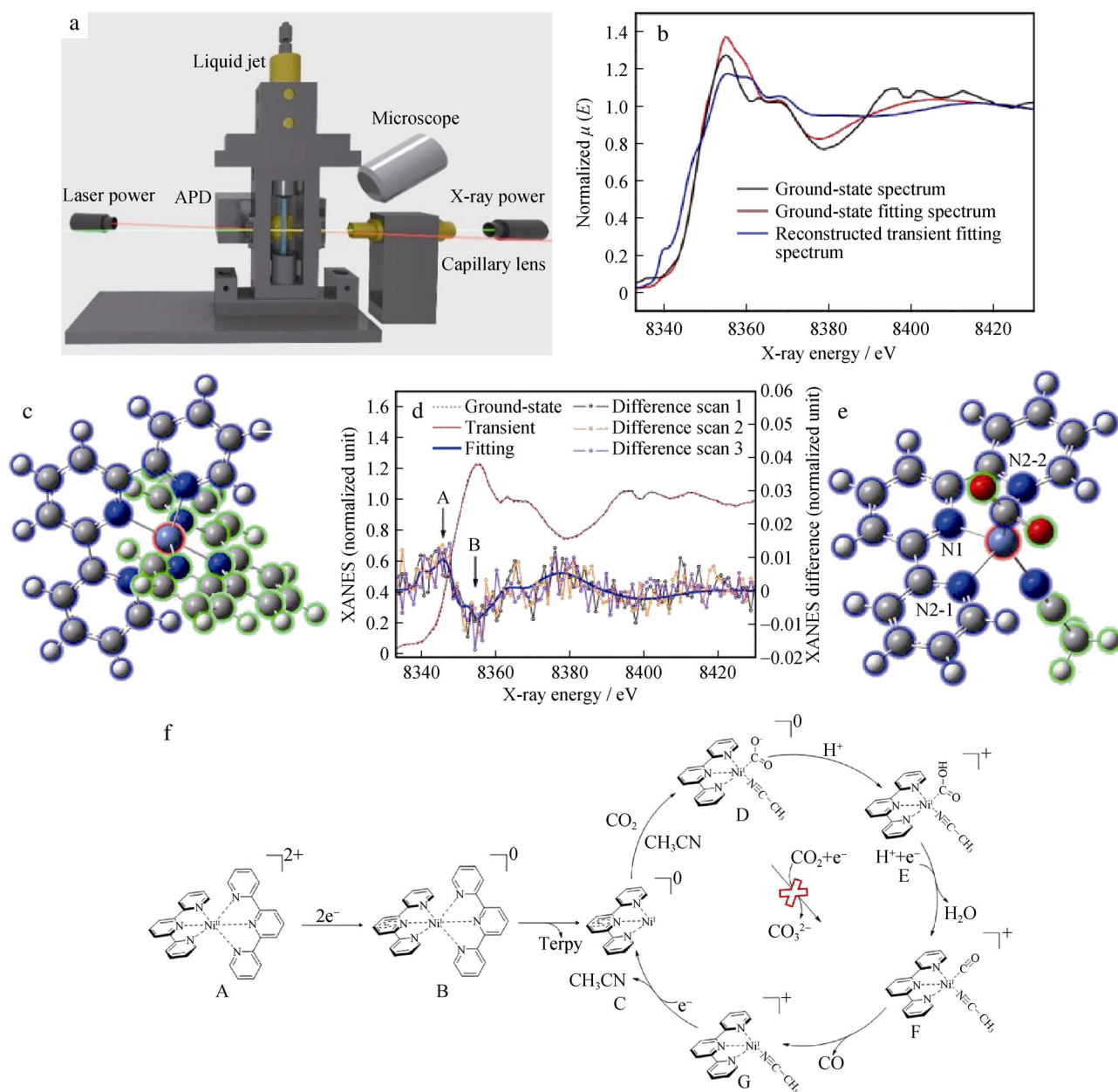

Fig. 1 Tracking mechanistic pathway of photocatalytic CO$_2$ reaction at Ni sites using operando time-resolved spectroscopy: a schematic illustration of TR-XAS; b experimental XANES spectra of Ni(II) complex; c six-coordinated Ni-N$_6$ octahedral configuration of Ni complex; d transient XANES spectra of Ni(II) complex; e penta-coordinated distorted tetrahedron configuration of Ni intermediate; f full reaction pathway for CO$_2$ reduction reaction catalyzed by [Ni(tpy)]$_0$ (Reproduced with permission from Ref. [17]. Copyright American Chemical Society)

catalyst molecules after the light source irradiation. Then, CO_2 and CH_3CN were bound to the active site of the catalyst. The catalyst was no longer a geometric model with Ni as the symmetry center.

Next, the authors proposed to measure the redox potential of each component in the model using electrochemical testing. By analyzing the reduction potentials of BIH and Ni(II) in the model, it could be concluded that there is a reduction quenching process in the catalytic reaction process. Combined with the research on the photoluminescence spectrum and luminescence lifetime, it was found that BIH had a quenching effect on Ni(II). This conclusion implied that the photoelectrons did not come directly from Ru(II) photosensitizer. The authors further used light transient absorption (OTA) spectroscopy to detect the effects of the addition of each component on the catalytic reaction. The addition of BIH results in a new absorption peak at 510 nm, which means that Ru(I) is formed by BIH, quenching the excited state * Ru(II). The addition of Ni(II) accelerated the consumption of Ru(I). Thus, the photoelectrons-induced Ni(II) to Ni(I) were derived from Ru(I). By studying the effect of the catalytic reaction between BIH and Ni(II), a cycle of Ru(II) is concluded: BIH quenches Ru(II) to form Ru(I), and then Ru(I) releases another photoelectron and turns into Ru(II). Finally, the author uses density functional theory (DFT) calculations to prove that the conversion of CO_2 to CO is through the dehydroxyl pathway. The coordination structure, electronic structure, charge dynamics and reaction free energy were systemic studied. According to these results, there action pathway can be proposed, as shown in Fig. 1F. After accepting two photo-generated electrons, A is converted into B. When combined with CO_2 and solvent CH_3CN molecules, B will lose the neutral terpyridine to form C. The next step is to protonate the coordination formed by the combination of CO_2 and the active Ni site and convert D to E, followed closely by the dehydroxyl reaction of CO to form intermediate product F. Finally, it turns into C and releases CO_2 and CH_3CN molecules.

In summary, the report by Xiong and co-workers provided exciting evidence, using TR-XAS firstly to explore the changes in the coordination environment of Ni catalysts, other spectroscopic techniques to explore the cycle of Ru(II) and the theoretical analyses of the carbon cycle to elaborate the complete reaction path. This discovery will encourage the future development of photocatalytic CO_2 reaction with high selectivity and activity.

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