

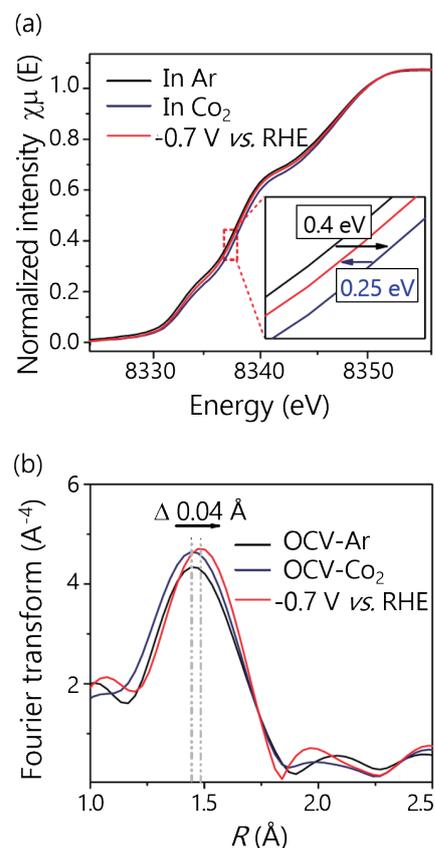
# Uncovering the Catalytically Active Site with X-rays

Electronic states of catalysts have given significant insight into CO<sub>2</sub> reduction reactions.

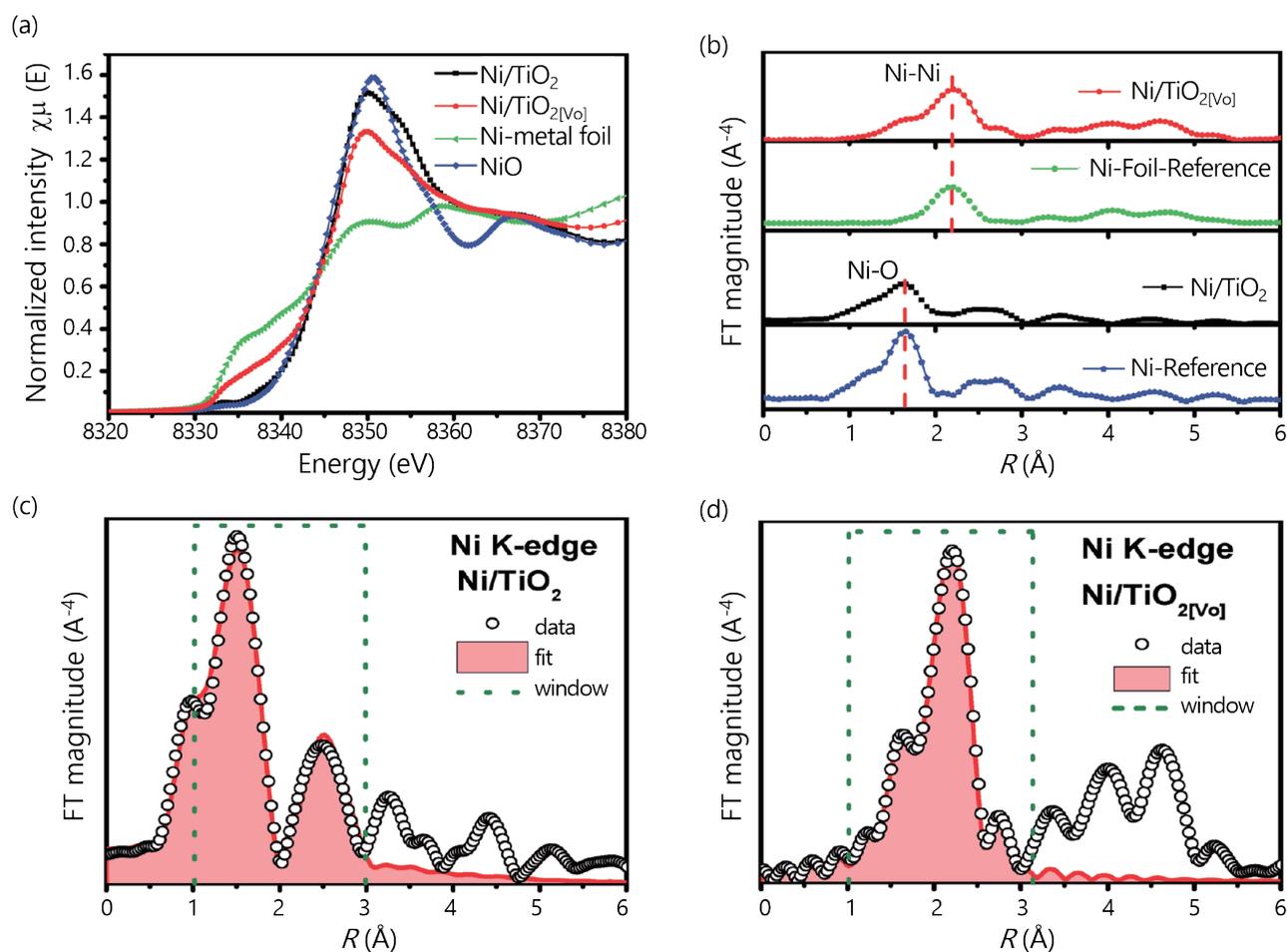
The reduction of CO<sub>2</sub> to a chemical fuel offers a promising strategy to manage the global carbon balance, but presents challenges for chemistry because of the lack of an efficient catalyst. One key challenge is to design a great catalyst that can bind and activate the CO<sub>2</sub> molecule with the least possible activation energy and produce selective hydrocarbon products. The development of improved catalysts with adequate activity and selectivity is hence still a long-term goal to realize their practical application. Single-atom catalysts with atomically distributed active metal centers have demonstrated maximum atom efficiency and excellent selectivity in several catalytic reactions because of the unique electronic properties of a single active site, and are thus expected to have a great potential to improve the performance of the CO<sub>2</sub> reduction. Furthermore, anatase TiO<sub>2</sub> and its hybrid catalysts have been extensively studied for CO<sub>2</sub> reduction because of their unique physicochemical properties, but the construction of perfect single-atom catalysts or TiO<sub>2</sub> hybrid catalysts remains a great challenge. More importantly, the atomic structure of the developed catalysts has remained elusive, which impedes an understanding of these catalysts and the further design of new catalysts for the CO<sub>2</sub> reduction.

Bin Liu (Nanyang Technological University) and his co-workers recently developed atomically dispersed nickel on nitrogenated graphene as an efficient and durable electrocatalyst for CO<sub>2</sub> reduction.<sup>1</sup> Employing X-ray absorption spectra *operando* at NSRRC beamline **SP12B1** of SPring-8, the authors clarified the details of the adsorption and activation of CO<sub>2</sub> on single-Ni-atom catalysts (**Fig. 1**). The Ni K-edge shifted approximately 0.4 eV to greater energy in CO<sub>2</sub>-saturated KHCO<sub>3</sub> solution under an open-circuit voltage bias relative to that in an Ar-saturated KHCO<sub>3</sub> solution. This effect indicates an increased Ni oxidation state, which probably results from delocalization of the unpaired electron in the 3d<sub>x<sub>2</sub>-y<sub>2</sub></sub> orbital and a spontaneous charge transfer from Ni(I) to the carbon 2p orbital in CO<sub>2</sub> to form a CO<sub>2</sub><sup>δ-</sup> species. During electrochemical CO<sub>2</sub> reduction, the Ni K-edge of single-Ni-atom catalysts shifted back to smaller energy, which indicates the recovery of the low-oxidation-state Ni after one cycle of CO<sub>2</sub> reduction. The intensity of the main signal at approximately 1.45 Å in the Fourier transform of the EXAFS spectrum (**Fig. 1(b)**) increased slightly, which was ascribed to a contribution from the Ni–C bond that overlapped with the Ni–N bond. The main signal shifted (~0.04 Å) to greater length during CO<sub>2</sub> reduction with the catalyst biased at -0.7 V vs. RHE, relative to that under an open-circuit voltage bias, which indicates an extension of the Ni–N bond. This extension is due to distortion of the Ni atoms from the graphene plane, and results from a redistribution of the electrons in the Ni 3d orbital between the four N ligands and the Ni–C bond (from adsorbed CO<sub>2</sub>).

Black TiO<sub>2</sub> loaded with Ni-nanoclusters with dual active sites for selective photocatalytic CO<sub>2</sub> conversion was also developed by Li-Chyong Chen (National Taiwan University) and Kuei-Hsien Chen (Academia Sinica).<sup>2</sup> Employing X-ray absorption spectra at **TLS 17C1** and **TLS 01C1**, these authors investigated how the chemical environment and its electronic interaction around the Ni site alter in the CO<sub>2</sub> reduction (**Fig. 2**); they found that the metallic Ni clusters are anchored on the black TiO<sub>2</sub>. A robust conjugation of this kind to assist the Ni clusters to coalesce



**Fig. 1:** X-ray absorption spectra *operando*. (a) Normalized Ni K-edge XANES spectra *operando* at various biases in KHCO<sub>3</sub> aqueous solution (0.5 M) at 23 °C under Ar or CO<sub>2</sub> at 1 bar. The inset shows the enlarged Ni K-edge XANES spectra. (b) Fourier-transform magnitudes of EXAFS spectra under open-circuit voltage bias in Ar (OCV-Ar) and CO<sub>2</sub> (OCV-CO<sub>2</sub>), and at -0.7 V vs. RHE, in which an extended Ni–N bond was detected. [Reproduced from Ref. 1]



**Fig. 2:** (a) X-ray absorption near-edge spectra at the Ni K-edge of Ni/TiO<sub>2</sub> and Ni/TiO<sub>2</sub>[Vo] catalysts. (b)  $k^3$ -weighted EXAFS data of the Ni K-edge and first-shell fits obtained from (c) Ni/TiO<sub>2</sub> and (d) Ni/TiO<sub>2</sub>[Vo]. [Reproduced from Ref. 2]

strongly with the TiO<sub>2</sub> provides a less resistive path suitable for rapid electron transfer. This conjugation hampers the aggregation of Ni clusters, thereby facilitating highly reactive sites on the surfaces. The anchored configuration induces a charge transfer from the TiO<sub>2</sub> conduction band to the NiO/Ni nanoclusters, which further up-shifts the  $d$ -band center of Ni, and thereby increases its CO<sub>2</sub> binding to the surface. This condition in turn favors the photocatalytic reduction of CO<sub>2</sub>, leading to the great activity and selectivity of the C<sub>2</sub>-molecule production.

In summary, the discoveries of single-Ni-atom catalysts and Ni-nanocluster-loaded black TiO<sub>2</sub> offer a unique insight into the geometry of the active site and structural transitions during CO<sub>2</sub> reduction, which will be essential for the development of future CO<sub>2</sub> catalysts. Furthermore, the ability to probe atomic structures of catalysts under conditions operando makes synchrotron-based X-ray spectra an important technique to provide valuable insight for issues related to catalysts. (Reported by Yan-Gu Lin)

This report features the work of (1) Bin Liu and his co-workers published in *Nat. Energy* **3**, 140 (2018); (2) Li-Chyong Chen and her co-workers published in *Small* **14**, 1702928 (2018).

#### TLS 01C1 SWLS – EXAFS

#### TLS 17C1 W200 – EXAFS

#### SP12B1 BM – Materials X-ray Study

- XANES, EXAFS
- Materials Science, Chemistry, Condensed-matter Physics, Environmental and Earth Sciences

#### References

1. H. B. Yang, S.-F. Hung, S. Liu, K. Yuan, S. Miao, L. Zhang, X. Huang, H.-Y. Wang, W. Cai, R. Chen, J. Gao, X. Yang, W. Chen, Y. Huang, H. M. Chen, C. M. Li, T. Zhang, and B. Liu, *Nat. Energy* **3**, 140 (2018).
2. T. Billo, F.-Y. Fu, P. Raghunath, I. Shown, W.-F. Chen, H.-T. Lien, T.-H. Shen, J.-F. Lee, T.-S. Chan, K.-Y. Huang, C.-I. Wu, M. C. Lin, J.-S. Hwang, C.-H. Lee, L.-C. Chen, and K.-H. Chen, *Small* **14**, 1702928 (2018).