Ru, accompanied by electron delocalization and electron transfer from Ru 3*d* orbitals to N_{ads} 2p orbitals, thus implementing activation. This activated N_2 can be reduced continuously via hydrogenation at applied potentials.

In summary, the authors developed a chemically activated MXene with rich Mo-deficit defect sites with spontaneous Ru atomic doping for high-performance NRR catalysis under ambient conditions. The specific mechanism of this excellent activity was unveiled through *operando* XAS measurements. This work opens an avenue to rational design of MXene-based electrocatalysts and highlights the atomic-doping engineering strategy to manipulate effectively the catalytic performance of electrocatalysts. (Reported by Yan-Gu Lin)

This report features the work of Yongwen Tan and his collaborators published in Adv. Energy Mater. ***10****, 2001364 (2020).*

TLS 01C1 SWLS – EXAFS

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

Reference

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Heterogeneous Metal-Metal and Metal-Oxide Interfaces of Nanocatalysts Enable CO_2 Reduction with High Performance

Sub-nanometer heterogeneous interface induces lattice strain and electronegativity gradient in neighboring local domains and thus enabling the high selectivity and activity of CO_2 reduction in nanocatalysts.

Mitigation of the global energy crisis and adverse climatic impacts (increasing emission of carbon dioxide, CO_2) relies on the implementation of a sustainable energy economy. In this context, catalytic transformations of CO_2 to fuel/chemical feedstocks is the greatest accomplishment to diminish the carbon emission by industry. The most effective techniques for CO_2 reduction (CO_2R) include thermal and electrochemical reactions that can respectively be adopted to recycle industrial exhaust gas and to the conversion of green energies. Regardless of the aformentioned techniques, metal-metal and metal-oxide interfaces in a single nanoparticle have been proved to be the most efficient geometric design among heterogeneous catalysts for CO_2R.

To this end, in thermal CO_2R, Tsan-Yao Chen from National Tsing Hua University, with the cooperation of Xin Tu (University of Liverpool, UK), Dai Sheng (East China University of Science and Technology, China), Kuan-Wen Wang (National Central University, Taiwan), Jr-Hau He (City University of Hong Kong, Hong Kong) and Chia-Hsin Wang (NSRRC), has recently developed a hierarchically structured bimetallic nanocatalyst (NC) comprising a metallic Pd-nanocluster adjacent to local tetrahedrally symmetric Ni-oxide and a thin layer of tetramethyl orthosilicate decoration (denoted as NiO_TPd-T) that was synthesized by sequential control of the metal-ion adsorption followed by wet chemical reduction on the carbon nanotube support at room temperature (**Fig. 1(a)**)[1]. By cross-referencing the results of the X-ray photoemission spectrum *in situ* (**Figs. 1(b) and 1(c)**), other X-ray spectroscopic and electron microscopic techniques, they confirmed the local synergetic collaboration induced at the interface between metallic Pd and Ni oxide, which enables the intermediate steps in the methanation of CO_2. Compared to a pure Pd NC, the NiO_TPd-T NC exhibited a superior yield of CH_4 production, 1905.1 $\mu mol/g_{catalyst}$ at 300 °C. Moreover, the NiO_TPd-T NC surpassed existing catalysts with the same loading and composition and of any geometric configuration. In this study, NSRRC beamlines **TLS 01C1** and **TLS 24A1** were used.

Furthermore, in electrochemical CO_2R, Dr. Hao-Ming Chen (National Taiwan University) and his co-workers developed silver(Ag)-modified copper (Cu) nanowires as effective electrocatalysts towards electrochemical CO_2 reduction (CO_2RR).[2] $Cu_{68}Ag_{32}$ nanowires as prepared demonstrated the best performance towards methane with Faradaic efficiency ~60%, which is nearly three times that of primitive Cu nanowires (**Fig. 2(a)**). Most importantly, it surpasses the most efficient catalysts for producing methane. Using XANES techniques *in situ* at NSRRC beamlines **TLS 01C1** and **TLS 01C2**, they unveiled the valence state of Cu at the potential range of forming a CuAg alloy and tracked the structural changes to establish a structure-performance relation.

In brief, both of these pioneer works provide a deep understanding of NC design based on metal-metal and metal-oxide heterojunctions for both thermal and electrocatalytic conversion of CO_2. (Reported by Tsan-Yao Chen, National Tsing Hua University)

This report features the works of (1) Tsan-Yao Chen and his collaborators published in J. Mater. Chem. A ***8****, 12744 (2020) and (2) Hao Ming Chen and his collaborators published in J. Am. Chem. Soc.* ***142****, 12119 (2020).*

TLS 01C1 SWLS – EXAFS
TLS 01C2 SWLS – X-ray Powder Diffraction
TLS 24A1 BM – (WR-SGM) XPS, UPS, XAS, APXPS

- XANES, EXAFS, XRD, XPS, UPS
- Materials Science, Chemistry, Surface, Interface and Thin-film Chemistry, Condensed-matter Physics

References

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2. C.-J. Chang, S.-C. Lin, H.-C. Chen, J. Wang, K. J. Zheng, Y. Zhu, and H. M. Chen, J. Am. Chem. Soc. **142**, 12119 (2020).

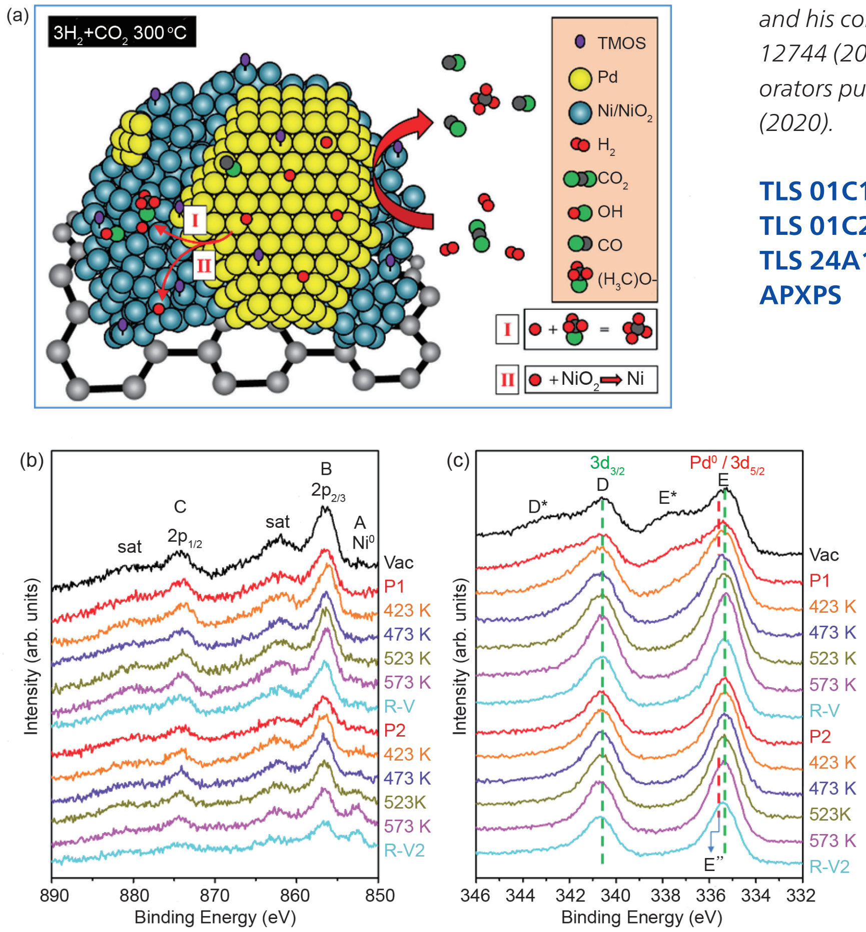

Fig. 1: (a) Schematic representation of NiO$_T$Pd-T NC. X-ray photoelectron spectra (APXPS) *in situ* at ambient pressure of NiO$_T$Pd-T at (b) Ni 2p and (c) Pd 3d regions. [Reproduced from Ref. 1]

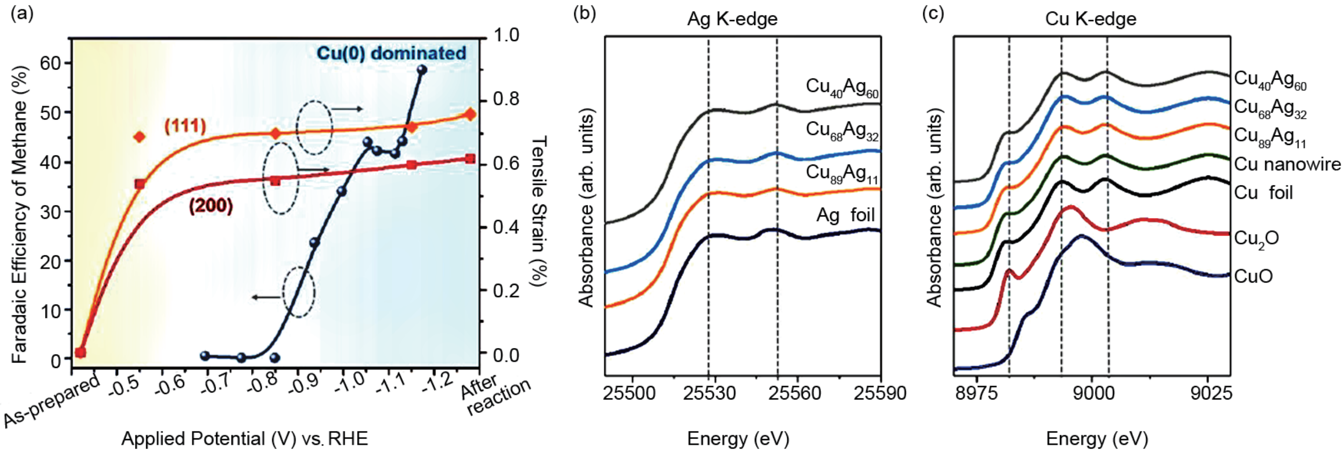

Fig. 2: (a) Faradaic efficiency of methane of a Cu$_{68}$Ag$_{32}$ catalyst and tensile strain at planes (111) and (200) caused by a CuAg alloy as a function of potential. XANES spectra of (b) Ag K-edge for silver-modified Cu nanowire samples and (c) Cu K-edge for Cu nanowires, silver-modified Cu nanowire samples and corresponding references. [Reproduced from Ref. 2]