Mechanistic Investigation of Urea Synthesis by Plasmon-Assisted N_2 and CO_2 co-electrolysis of Silver Nanoparticles on Heterojunctions

Leandro A. Faustino[1], Leonardo D. de Angelis[1], Eduardo C. de Melo[1], Giliandro Farias[1], Egon C. dos Santos[1], Caetano R. Miranda[1], Ana G. Buzanich[3], Roberto M. Torresi[1], Paulo F. M. de Oliveira[1], Susana I. Cordoba de Torresi[1]
[1]Universidade de São Paulo, Av. Prof. Lineu Prestes 748, 05360-050, São Paulo – SP, Brazil
[3]Federal Institute of Materials Research and Testing, Richard-Willstaetter-Str. 12, 12489 Berlin, Germany
e-mail address: leandrofaustino@usp.br and storresi@iq.usp.br

The N_2 and CO_2 co-electrolysis have attracted attention as an alternative to the energy intensive process for urea synthesis. Here we reported the contribution of localized surface plasmon resonance (LSPR) of Ag NPs supported on heterojunctions, Ag@$BiVO_4$/$BiFeO_3$, during the N_2 + CO_2 co-electrolysis. Our results demonstrated that exciting in the LSPR region of Ag NPs the Faradaic Efficiency and urea yield rate was improved with a reduced overpotential, 24.4% and 19.2 μmol h^{-1} g^{-1} at +0.1 V *vs* RHE compared to 9.4% and 9.6 μmol h^{-1} g^{-1} at -0.2 V *vs* RHE under dark conditions. Further *in situ* FTIR-IR investigations, Fig. 1A, demonstrated that under dark and N_2 + CO_2 atmosphere conditions, no huge signals related to nitrogen-intermediates were observed, otherwise a strong adsorption of H_2O over catalyst surface was observed leading to HER. Under LSPR and N_2 + CO_2 conditions, signals related to nitrogen-intermediates were observed at 3320, 3131 and 1337 cm^{-1} related to the urea formation. In relation to H_2O species, an opposite behavior was observed, revealing that under LSPR conditions, H_2O species are not easily absorbed over catalyst surface and then HER is suppressed.

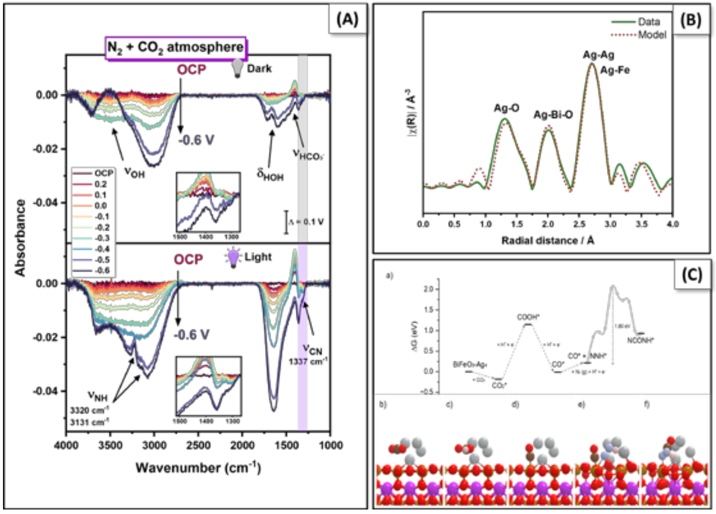

Figure 1. (A) *In situ* FTIR-RAS experiments under N_2 + CO_2 atmosphere under dark condition (top) and upon laser irradiation (λ = 455 nm) (bottom) using Ag@$BiVO_4$/$BiFeO_3$ in 0.2 mol L^{-1} $KHCO_3$, (B) Fourier-Transformed Ag-K edge k^2-weighted EXAFS spectra of Ag@$BiVO_4$/$BiFeO_3$ and (C) free energy profile until the coupling reaction to NCONH* over $BiFeO_3$-Ag_4 surface

As the Ag@$BiVO_4$/$BiFeO_3$, prepared mechanochemically, possesses a complex structure, X-Ray Absorption Spectroscopy (XAS) experiments were carried out, Fig. 1B, to understand its structure and identify the possible catalytic sites involved in the urea electrosynthesis. XAS data showed that in addition to the expected Ag-Ag scattering for Ag species, other domains are present in the catalyst structure, such as Ag-O, Ag-Bi-O and Ag-Fe. Theoretical calculations considering different types of possible structures, revealed that a cluster $BiFeO_3$-Ag_4 plays an important role in the free energy profile for the C-N coupling to give NCONH*, Fig. 1C. In addition, the theoretical calculations agree with XAS data and intermediates observed on *in situ* FTIR-IR experiments.

Acknowledgments

This work is supported by FAPESP (2021/00675-4, 20/15230-5, 2022/04604-7, 24/13493-0) and RGCI/ Shell do Brasil.