

## In situ Spectroscopic Investigation of Electrochemical CO<sub>2</sub> Reduction Reaction on Cu/M Surface Alloy Nanocubes (M=Pt, Ir)

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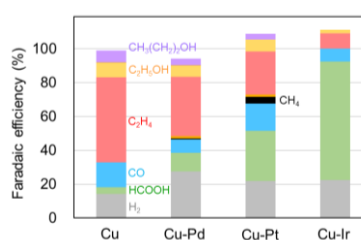
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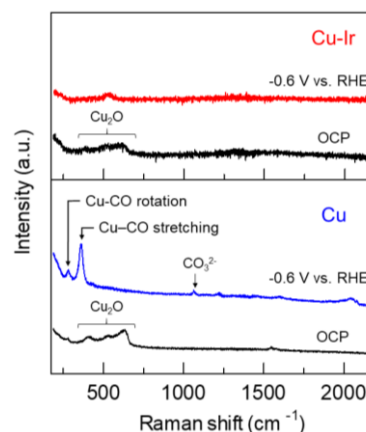
Cu is a useful catalyst for the electrochemical reduction of CO<sub>2</sub> to several chemicals including CO, C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>5</sub>OH.<sup>1</sup> In order to control the product selectively on Cu, we previously prepared novel Cu/M surface alloy nanocubes (Cu/M NCs, M=Pt, Ir), and conducted electrochemical CO<sub>2</sub> reduction reactions (CO<sub>2</sub>RR). While Cu NCs mainly produced ethylene, Cu/Ir NCs showed high selectivity for formic acid (Fig. 1).<sup>2</sup> Since monometallic Ir mainly produced H<sub>2</sub>, the CO<sub>2</sub>RR properties of Cu NCs were significantly altered by alloying with Ir. In this study, we investigated the local structures and intermediates of Cu/M NCs during the reaction using in situ X-ray absorption fine structure (XAFS) and Raman spectroscopy to elucidate the reaction mechanism.

The results of in-situ XAFS measurements showed that the Cu-Ir surface alloy structure remained stable under an applied potential of -0.6 V vs. RHE. Fig. 2 shows in situ Raman spectra of Cu NCs and Cu/Ir NCs recorded at open circuit potential (OCP) and -0.6 V, respectively. At -0.6 V for Cu NCs, peaks corresponding to CO adsorbed on Cu were detected. These peaks, observed at 280 cm<sup>-1</sup>, 360 cm<sup>-1</sup>, and 2042 cm<sup>-1</sup>, represent the restricted rotation of adsorbed CO, Cu-CO stretching, and C-O stretching vibrations, respectively.<sup>3</sup> These CO species serve as important intermediates in ethylene production. In contrast, no peaks associated with adsorbed CO on Cu were observed at -0.6 V for Cu/Ir NCs. This result suggests that the product pathway of Cu is modified by alloying with Ir, leading to the formation of formic acid via a mechanism that does not involve the CO intermediate on the Cu/Ir surface. The detailed mechanism is further analyzed in conjunction with the results of the Cu-Pt and Cu-Pd systems.

1) Y. Hori, H. Wakebe, T. Tsukamoto, O. Koga, *Electrochim Acta.*, **1994**, 39, 1833. 2) H. Kobayashi, S. Hikino and M. Yamauchi, *The 104<sup>th</sup> CSJ Annual Meeting 2024*, A1458-4pm-06. 3) a) C. Chunjun., *et al*, *Chem. Sci.*, **2021**, 12, 5938. b) J. Gao, *et al*. *J Am Chem Soc.*, **2019**, 141, 18704.



**Fig. 1** Faradaic efficiencies for electrochemical CO<sub>2</sub> reduction on Cu cubes, Cu-Pd NC, Cu-Pt NC and Cu-Ir NC.



**Fig. 2** In-situ Raman spectra of Cu NCs and Cu/Ir NCs recorded at OCP and -0.6 V vs. RHE under CO<sub>2</sub> gas flow, respectively.