Electronic Supplementary Material (ESI) for Chemical Communications.

Electronic Supplementary Information

Explosive Enantiospecific Decomposition of Aspartic Acid on Cu Surfaces

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SI.1. Experimental Methods

Sample preparation, analysis and TPR spectra were performed under UHV conditions in chambers equipped with Ar^+ ion guns for cleaning of Cu single crystal surfaces and LEED optics for determination of their crystallographic orientation. The Cu single crystal samples were mounted on sample manipulators that allowed resistive heating to >1000 K and cooling with liquid nitrogen to <100 K. The temperature was measured using a chromel-alumel thermocouple spot-welded to the edge of the crystal. Before each measurement, the Cu sample surface was cleaned by first annealing at 1000 K in 5×10^{-10} Torr of O_2 for 300 s followed by cycles of Ar^+ sputtering (10 μA, 1.5 keV) at 750 K for 900 s. The sample was then annealed at 1000 K for 600 s.

D- and *L*-Asp were deposited onto the sample surfaces using home built sublimation sources. The Asp powder was contained in glass vials with ~6 mm inside diameter and wrapped with resistive heating wire. These were heated at constant temperatures of 370 – 400 K in order to generate fluxes that would saturate the Cu surface using exposures of ~20 min. The exposure times were controlled using a shutter positioned in front of the sublimation source. TPRS was conducted by positioning the sample in front of the aperture to a mass spectrometer and heating the Cu crystal at 1 K/s using a computer to control the temperature. Isothermal TPRS was conducted by heating the crystal to the desired temperature at 1 K/s and then holding the temperature constant as long as was needed. The mass spectrometer was capable of collecting signals at up to 16 masses simultaneously.

XP spectra were collected using a ThermoFisher ThetaProbe™. Spectra were taken using a 400 μm diameter monochromated x-ray spot and collected using an analyzer pass energy of 40 eV.

The Cu single crystals were obtained from Monocrystals Co. *L*-Asp and 1-^{13}C-*L*-Asp (>99% purity) were obtained from Sigma-Aldrich Co. 1,4-$^{13}C_2$-*L*-Asp and 3,4-$^{13}C_2$-*L*-Asp (> 99% purity) were obtained from Cambridge Isotopes Ltd. The *L*-Asp powders were purified of low vapor pressure contaminants by heating to ~400 K for several hours under UHV conditions prior to use.

SI.2. Core level binding energies for L-Asp/Cu(110)

Table S1. Core level binding energies for zwitterionic multilayer Asp and doubly-deprotonated monolayer Asp on Cu(110).

Core level	Atom	Adsorbed Species	
		$^{-}O_2CCH(NH_3^+)CH_2CO_2H$	$O_2CCH(NH_2)CH_2CO_2$
C 1s	CH_2	285.8 eV	285.1
	$CH(NH_2)$		286.0
	$CH(NH_3^+)$	286.9	
	COO	288.6	288.0
	COOH	289.5	
N 1s	NH_2		299.8
	NH_3^+	402.2	
O 1s	CO_2^-	532.0	531.4
	CO_2H	533.2	

SI.3. Chemical State of L-Asp/Cu(111)

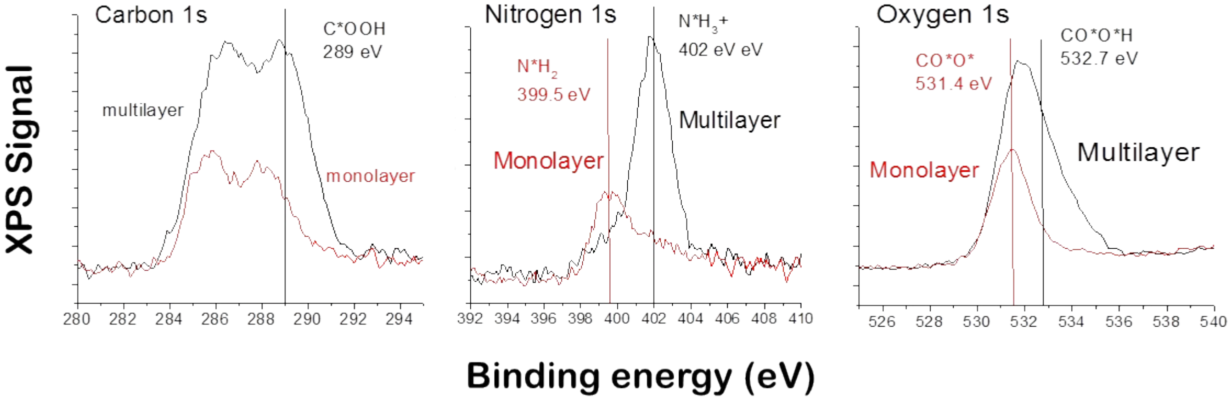

Figure SI1. C 1s, N 1s, and O 1s XPS spectra of *L*-Asp on Cu(111). The spectra for the multilayer (~3 ML) adsorbed at 300 K and the saturated monolayer prepared by annealing to 405 K are plotted in the same panels. The absence of the features assigned to NH_3^+ and COOH in the multilayer indicates that the monolayer is present in the doubly deprotonated state, $-O_2CCH(NH_2)CHCO_2-$.

SI4. -$O_2CCH(NH_2)CH_2$- decomposition intermediate species on Cu(110)

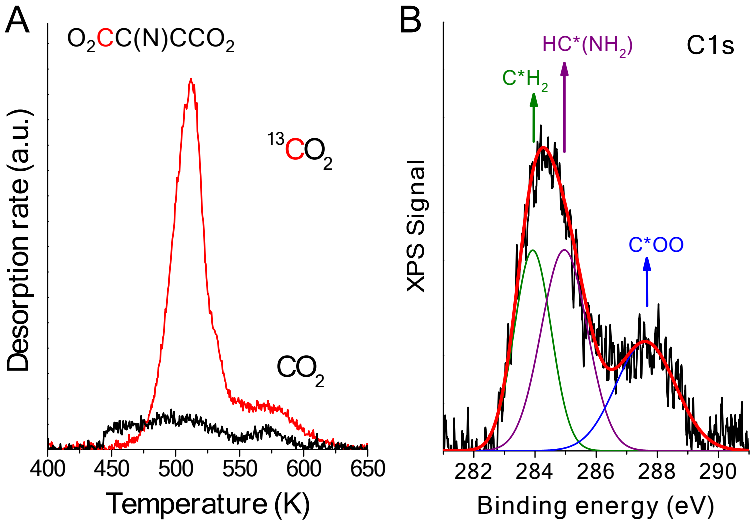

Figure SI2. TPRS and XPS of the -$O_2{}^{13}CCH(NH_2)CH_2$- decomposition intermediate prepared by exposure of the Cu(110) surface at 470 K to 1-^{13}C-*L*-Asp. A) The TPR spectra obtained by monitoring *m/z* = 44 (CO_2) and 45 ($^{13}CO_2$) demonstrate~~s~~ that the C3-C4 bond is cleaved during adsorption eliminating CO_2. The species remaining on the surface contains the -$O_2{}^{13}C$- group. B) The C1 XP spectrum reveals the presence of the -CH_2- and -$CH(NH_2)$- groups in the adsorbed intermediate. The peak associated with the -CO_2- groups is reduced by ~50% relative to its intensity in the biaspartate species (Figures 2 and SI1). These data are consistent with formation of a -$O_2{}^{13}CCH(NH_2)CH_2$- intermediate on the surface.