Plasma-promoted reactions of the bimetallic anions CuNb成年人与 dinitrogen and subsequent reactions with carbon dioxide: formation of C–N bonds

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1. Additional time-of-flight (TOF) mass spectra. (pages S3, S4 and S7)
2. Additional density functional theory results. (pages S2, S5, S6 and S8)
More calculated details:

\[ v_1 = \sqrt{\frac{3kT}{m_1}} = \sqrt{\frac{3 \times 1.38 \times 10^{-23} \times 298}{185 \times 1.66 \times 10^{-27}}} = 200 \text{ m/s} \]

\[ v_2 = \sqrt{\frac{\gamma kT}{m_2}} = \sqrt{\frac{1.304 \times 1.38 \times 10^{-23} \times 298}{44 \times 1.66 \times 10^{-27}}} = 271 \text{ m/s} \]

\[ v = (v_1 + v_2) = (200 + 271) = 471 \text{ m/s} \]

\[ m_1 = m_{(CuNbN^-)}, m_2 = m_{CO_2} \]

\[ k: \text{Boltzmann constant;} \]

\[ \gamma: \text{Adiabatic Index (}\gamma_{CO_2} = 1.304); \]

\[ T = 298 \text{ K} \]
**Fig. S1.** TOF mass spectra of CuNb\(^-\) anions reacting with 20% N\(_2\) under plasma atmosphere provided by different laser power. The laser flash-lamp pulse energy at 12.5, 14.3, 22.9 and 28.4 mJ, respectively.
Fig. S2. Variation of relative intensities of the reactant and product ions for the reactions of CuNbN$_2^-$ with CO$_2$ pressures. The solid lines are fitted to the experimental data points with the approximation of the pseudo-first-order reaction mechanism.
Fig. S3. DFT-calculated structures and relative energies of (a) CuNbN₂⁻, (b) CuNbNO⁻, (c) NbN₂CO⁻, and (d) CuNb⁺ at the B3LYP/6-311+G*, aug-cc-pVTZ-pp and def2-TZVPD level of theory. In panel c, CCSD(T)-calculated structures and relative energies of (c) ¹IA19 and ¹IA20 are given parentheses. The point group is given under each structure. The superscripts indicate the spin states. The zero-point vibration corrected energies (ΔH₀K in eV) of each structure are given.
Fig. S4. B3LYP-D3-calculated PESs for the reaction of CuNbN$_2^-$ (3I2A) with CO$_2$. Zero-point vibration-corrected energies ($\Delta H_{0K}$ in eV) of the reaction intermediates, transition states, and products with respect to the separated reactants are given. The superscripts indicate the spin states.
Fig. S5. Time-of-flight mass spectra for the reactions of mass-selected CuNb− cluster with (a) He, and (b) N₂. The reaction time is about 14 ms, and the effective reactant gas pressures are shown.
Fig. S6. B3LYP-D3-calculated PESs for the reaction of CuNb\(^-\) with N\(_2\). Zero-point vibration-corrected energies (\(\Delta H_{0K}\) in eV) of the reaction intermediates, transition states, and products with respect to the separated reactants are given. The superscripts indicate the spin states.