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Unveiling CO_2 Electrocatalytic Mechanism in Ionic Liquids via Real-Time AFM and Voltammetry

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Contents:

1. Materials and methods
2. Experimental details
   2.1 Ionic liquid nanomembranes preparation
   2.2 Atomic force microscopy measurements
   2.3 Voltammetry measurements
3. Additional data

1. Materials and methods

Methanol (Sinopharm Chemical Reagent Co., Ltd, 99.8%, HPLC grade), used as solvents for ionic liquid nanomembranes preparation. Concentrated sulfuric acid (H_2SO_4, AR grade), hydrogen peroxide (H_2O_2, AR grade), ethyl alcohol (C_2H_5OH, AR grade) and acetone (CH_3COCH_3, AR grade) were purchased from Sinopharm Chemical Reagent Co., Ltd. 1-Butyl-3-methylimidazolium hexafluorophosphate ($BMIPF_6$, > 99%), 1-butyl-3-methylimidazolium dicyanamide (BMIDCA, > 99%) and 1-butyl-3-methylimidazolium nitrate ($BMINO_3$, > 99%) were purchased from IoLiTec. All the ionic liquids were stored in an argon-filled glove box (Vigor, H_2O < 0.1 ppm, O_2 < 0.1 ppm) and evacuated with a pump to remove water and oxygen before used. Mica (Tedpella V-1 level) used in this work were purchased from EMS.

2. Experimental details

2.1 Ionic liquids nanomembrane preparation

Ionic liquids were initially dissolved in methanol to form a 0.1 wt‰ concentration solution. Subsequently, a 5 μL aliquot of this solution was deposited onto a freshly cleaved mica substrate (8 mm × 8 mm dimension). The specimen was then subjected to controlled drying under an inert gas atmosphere. Following complete evaporation of the methanol solvent, ionic liquid residues were immobilized on the mica surface. This solvent removal process facilitated the self-assembly of ionic liquid nanomembranes, manifesting as either monolayer or multilayer configurations, via synergistic interactions between the ionic liquid components and the mica substrate surface.

2.2 Atomic force microscopy measurements

In situ atomic force microscopy measurements of ionic liquid nanomembranes were accomplished on a JPK Nano Wizard Sense scanning probe microscope (Bruker Corp.) equipped with a protective cover by AC mode with a silicon probe (force constant of 1.5-5.5 N/m, resonance frequency of 75-90 kHz). Carbon dioxide and nitrogen were purchased from Linde Gas Co., Ltd., Xiamen, China. All experiments were performed at room temperature (ca. 25◦C).

2.3 Voltammetry measurements

Electrochemical measurements were performed using an electrochemical workstation (AUTOLAB PGSTAT128N, Metrohm, Switzerland), with glassy carbon (GC) and gold polycrystalline (Au) electrode as the work electrode, a saturated calomel electrode (SCE) as the reference electrode, and a Pt wire as the counter electrode. Prior to each measurement, the work electrodes were required to undergo a standardized mechanical polishing protocol: beginning with sequential polishing using 1, 0.3, and 0.05 μm alumina powder suspensions (3 minutes per grade), followed by thorough rinsing with ultrapure water after each polishing step. Subsequently, the electrodes were subjected to two consecutive 5-minute ultrasonic cleaning cycles in deionized water to eliminate residual particulates, and finally dried under a nitrogen stream to ensure complete removal of surface moisture prior to testing.

3. Additional data

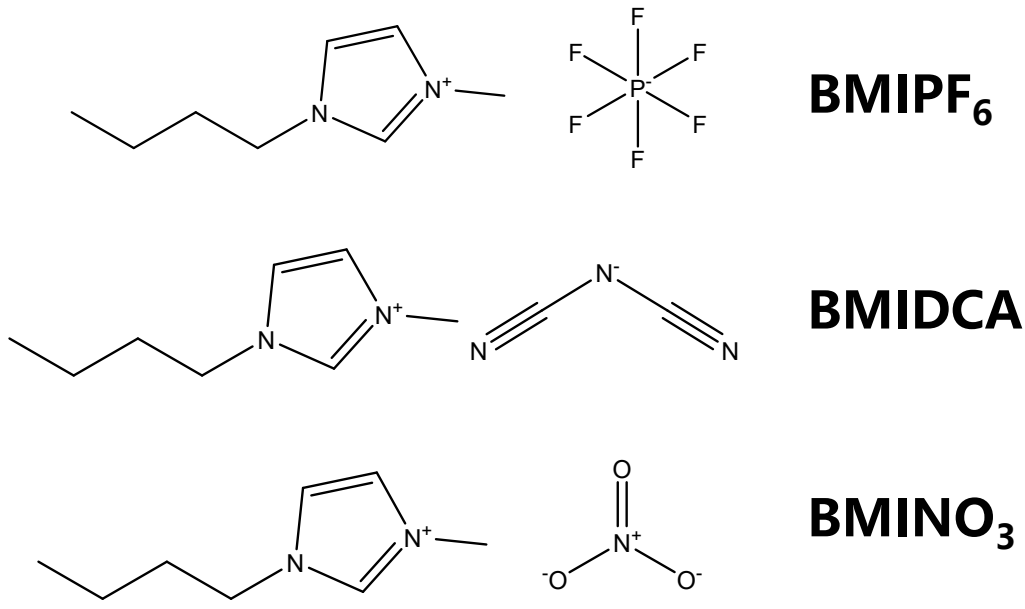

Fig. S1 Structural formulas of ionic liquid cation and anions used in this work.

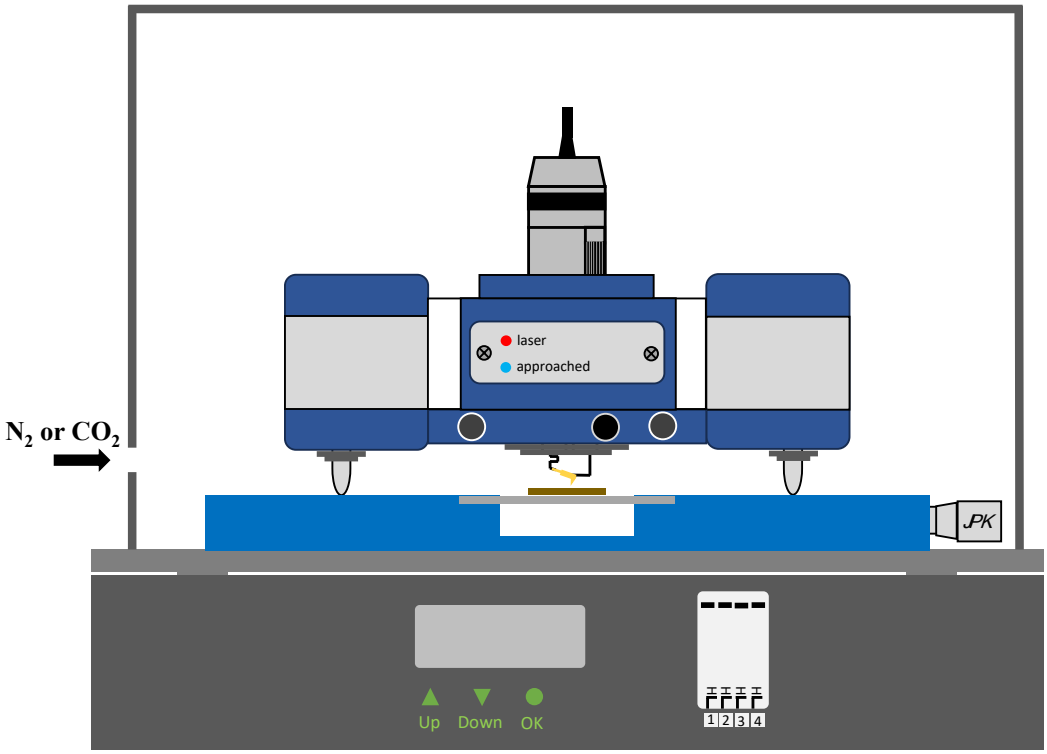

Fig. S2 Schematic diagram of atmosphere control for *in situ* AFM experiment.