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Supplementary Information

Formation of Ammonium Ions by Electrochemical Oxidation of Urea with a Boron-doped Diamond Electrode

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Experimental Details

1. Materials

Urea and sodium chloride were purchased from FUJIFILM Wako Pure Chemicals Corporation (Osaka, Japan) and used without further purification.

2. Decomposition of Urea

Electrochemical experiments were conducted in an H-type cell consisting of two glass half cells, as described in our previous study (N. Suzuki *et al.*, *RSC Adv.,* 2020, **10***,* 1793 - 1798). One half cell contained the BDD working electrode (hereafter called the reaction cell) and the other contained the Pt counter electrode (hereafter called the counter cell). When the photocatalyst was used together with the BDD electrode, a Kr-Br excimer lamp producing 207-nm UV light (ORC Manufacturing Co., Ltd (Machida, Tokyo, Japan)) and mesoporous TiO_2/BDD photocatalyst were also placed in the reaction cell. The fabrication process of the photocatalyst was described in our previous paper (N. Suzuki *et al.*, *Molecules*, 2018, **23**, 3095). The two cells were connected with a Nafion® NRE-212 membrane (Sigma-Aldrich (St. Louis, MO, US)). A schematic of the experimental setup is shown in **Figure 1**.

Urea solution (2 wt%) was prepared using 1 wt% NaCl aqueous solution as the solvent. The concentration of urea and urea/NaCl ratio were consistent with those of urine. Urea solution (50 mL) was poured into the reaction cell and 1 wt% NaCl aqueous solution (50 mL) was poured into the counter cell. The BDD electrode (and mesoporous TiO_2/BDD photocatalyst) were positioned horizontally and a constant current of 75 mA was applied to the BDD electrode to produce reactive oxygen species by water electrolysis. When the photocatalyst was used, 2.0 mW/cm^2 of 207-nm UV light from an excimer lamp (ORC Manufacturing Co., Ltd) was irradiated onto the TiO_2/BDD photocatalyst through a quartz sample tube. The glass cell was capped with a silicone rubber cap and Teflon tape to prevent evaporation during the experiments. Aliquots of the urea solution (1 mL) for further chemical analysis were collected several times during the experiment by opening the cap. The experiment was conducted at room temperature. During the test, the urea solution was constantly stirred.

3. Chemical Analysis

The concentration of urea in the collected samples was evaluated by high-performance liquid chromatography (HPLC; LC-2010, Shimadzu (Kyoto, Japan)) using an Xterra MS C 18 column (Waters (Milford, MA, US)). The measurement wavelength, column temperature and flow rate were 270 nm, 25 °C, and 0.5 mL/min, respectively. The mobile phase consisted of 0.25 M acetic acid (Solvent A) and acetonitrile (Solvent B) and the A:B ratio (7:3) was kept constant during the measurement.

The concentrations of ammonium (NH_4^+), nitrite (NO_2^-) and nitrate (NO_3^-) ions in the collected samples were evaluated by ion chromatography (Dionex ICS-1100, Thermo Fisher Scientific (Waltham, MA, US)) using Dionex IonPac CS12A-8 μm (Thermo Fisher Scientific) and Dionex IonPac AS12A (Thermo Fisher Scientific) columns for cations and anions, respectively.

Aqueous solutions of methanesulfonic acid (18 mmol/L) and a mixture of Na_2CO_3 (2.7 mmol/L) and $NaHCO_3$ (0.3 mmol/L) were used as the eluents for cations and anions, respectively. The column temperature was set to 30 °C for both cations and anions and the flow rate was 1.0 and 1.5 mL/min for cations and anions, respectively. Dionex ERS500 electrolytically regenerated suppressor was used to decrease the electric conductivity of the eluent and improve the sensitivity to target ions. The suppressor current was set to 30 and 60 mA for cations and anions, respectively.

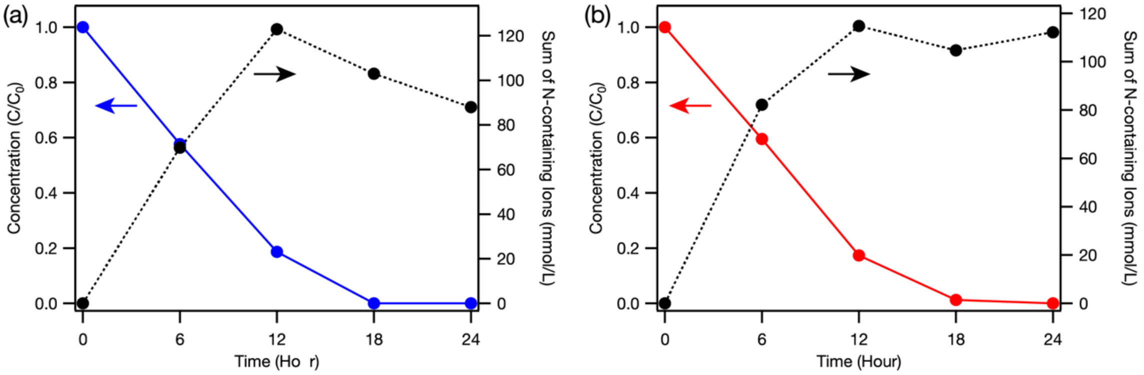
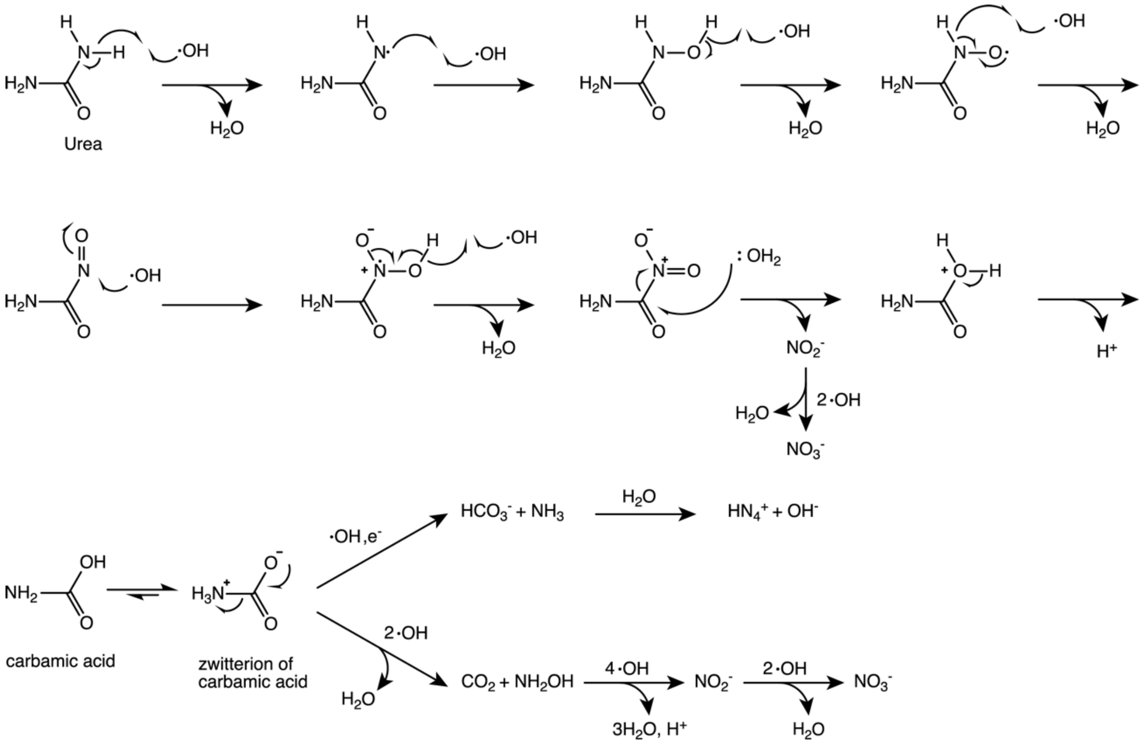


Figure S1. Comparison of the time dependence of urea concentration estimated from HPLC (a) with and (b) without photocatalytic reaction (i.e., Figure 2). C and C_0 are the remaining and initial urea concentrations, respectively. Sum of nitrogen containing ions measured with ion chromatography is also included.



Scheme S1. Urea oxidation mechanism induced by hydroxyl radicals proposed by Park *et al.* (*Environ. Sci. Pollut. Res.*, 2019, **26**, 1044-1053). Reprinted by permission from Springer Nature, copyright (2017).