Electronic Supplementary Material (ESI) for Dalton Transactions

Preparation and Formation Mechanism of a *n*-Butylammonium/MnO_2 Layered Hybrid via a One-Pot Synthesis under Moderate Conditions

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Ion-exchange synthesis of *n*-butylammonium/MnO_2 (m-C4/MnO_2)

Synthesis of K/MnO_2: Potassium-type birnessite (K/MnO_2) was synthesized according to the literature.[1] To 9 mL of 0.5 M $KMnO_4$ (Wako, 99.3%) was added 1 mL of 0.05 M HNO_3 (Nacalai Tesque, GR) in a 60 mL Teflon vessel. The vessel was sealed in a stainless steel autoclave; then the solution was subjected to mild hydrothermal treatment at 170 °C for 4 days under autogenous pressure. After cooling to room temperature, the resulting black crystallites were separated by filtration, washed with *ca.* 50 mL of distilled water, and then dried overnight *in vacuo* (0.53 g). The K/Mn ratio was estimated to be 0.31 on the basis of EDS, showing the sample to be pure.

Synthesis of H/MnO_2: Typically, 0.52 g of K/MnO_2 was added into 100 mL of 1 M HCl (Aldrich, 99.999%), and the suspension was stirred at room temperature for a week. The resulting blackish brown powder was separated by filtration, washed with *ca.* 50 mL of distilled water, and then dried overnight *in vacuo* (0.45 g). The K/Mn ratio was estimated to be 0.04 on the basis of EDS, indicating that about 90% of potassium ions were replaced by protons.

Synthesis of m-C4/MnO_2: Typically, 0.40 g of H/MnO_2 was added into 100 mL of distilled *n*-butylamine, and the suspension was stirred at room temperature for a week. The resulting blackish brown power was separated by filtration, washed with *ca.* 50 mL of distilled water, and then air-dried overnight (0.68 g). The amount of residual potassium remains almost unaltered by the acid-base reaction. Elemental analysis, in support of EDS, indicates the composition of (*n*-butylammonium)$_{0.17}K_{0.04}MnO_2 \cdot 0.3H_2O$ (Anal. Calcd for $C_{0.68}H_{2.64}K_{0.04}Mn_1N_{0.17}O_{2.3}$: C, 7.67; H, 2.50; N, 2.24%. Found: C, 7.64; H, 2.86; N, 2.32%), in which the formal valence on Mn (+3.79) is consistent with that of C4/MnO_2 obtained by the single-step approach.

Reference

(1) R. Chen, P. Zavalij, M. S. Whittingham, *Chem. Mater.* 1996, **8**, 1275.

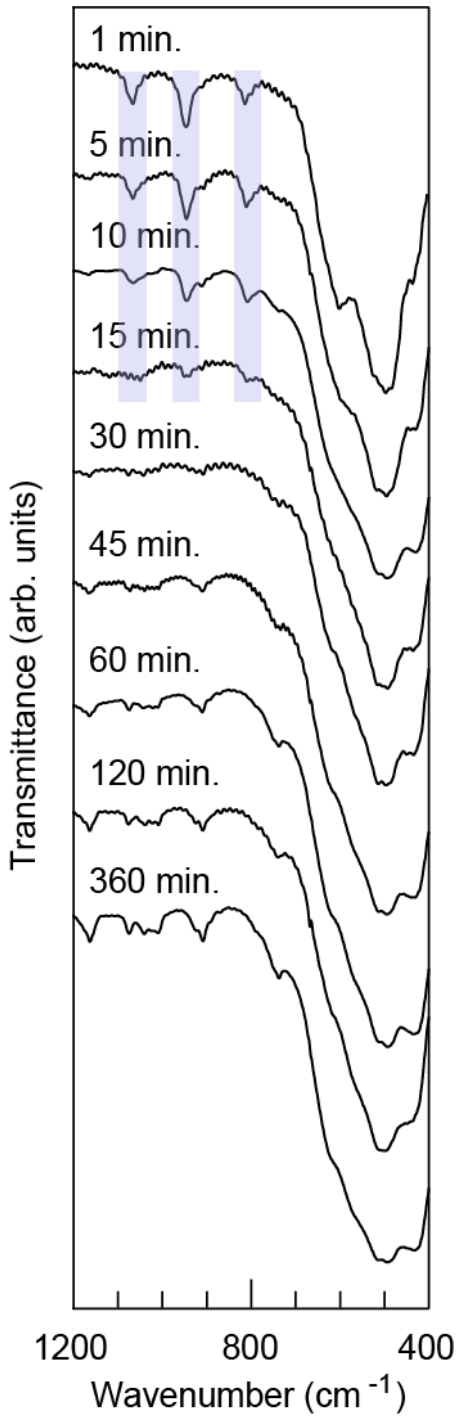

Figure S1. IR spectra of the products obtained by one-pot reaction with each reaction time. Three bands at 821, 955, and 1073 cm^{-1}, and two bands at 499 and 611 cm^{-1} corresponds to hydrogen-bonded O–H deformation vibration, and Mn–O vibration in *β*-MnOOH. For ≥ 30 minutes, the additional peaks between 800 to 1200 cm^{-1} correspond to interlayer *n*−butylammonium.

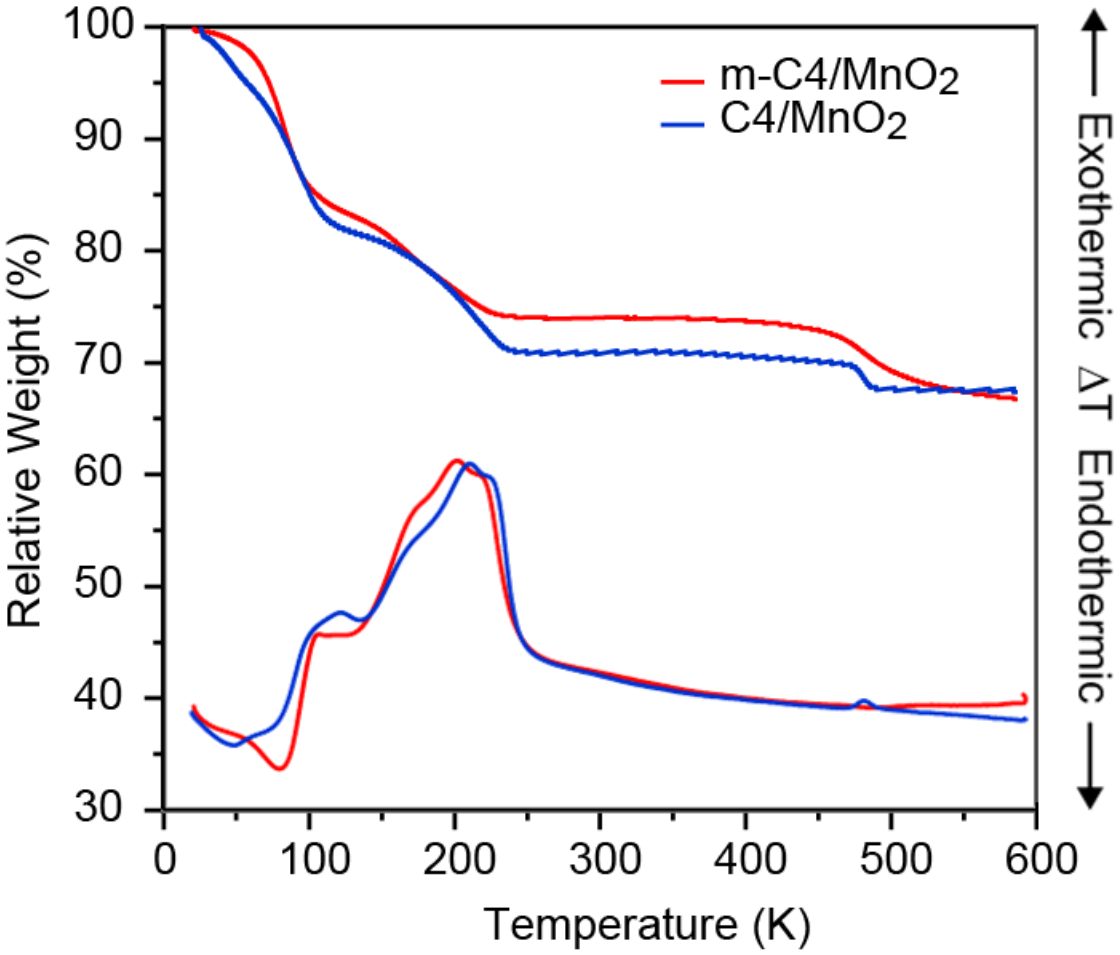

Figure S2. TG-DTA curves of $C4/MnO_2$ and $m\text{-}C4/MnO_2$. Based on the assumption that the first weight loss (17.6 % for $C4/MnO_2$ and 15.8 % for $m\text{-}C4/MnO_2$) and second weight loss (11.3 % $C4/MnO_2$ and 10.0 % $m\text{-}C4/MnO_2$) are due to the elimination of H_2O molecules and the combution of n-butylammonium cations respectively, we can estimate the chemical formulas as $(\text{n-butylammonium})_{0.19}MnO_2 \cdot 1.2H_2O$ for $C4/MnO_2$ and $(\text{n-butylammonium})_{0.16}MnO_2 \cdot 1.0H_2O$ for $m\text{-}C4/MnO_2$.

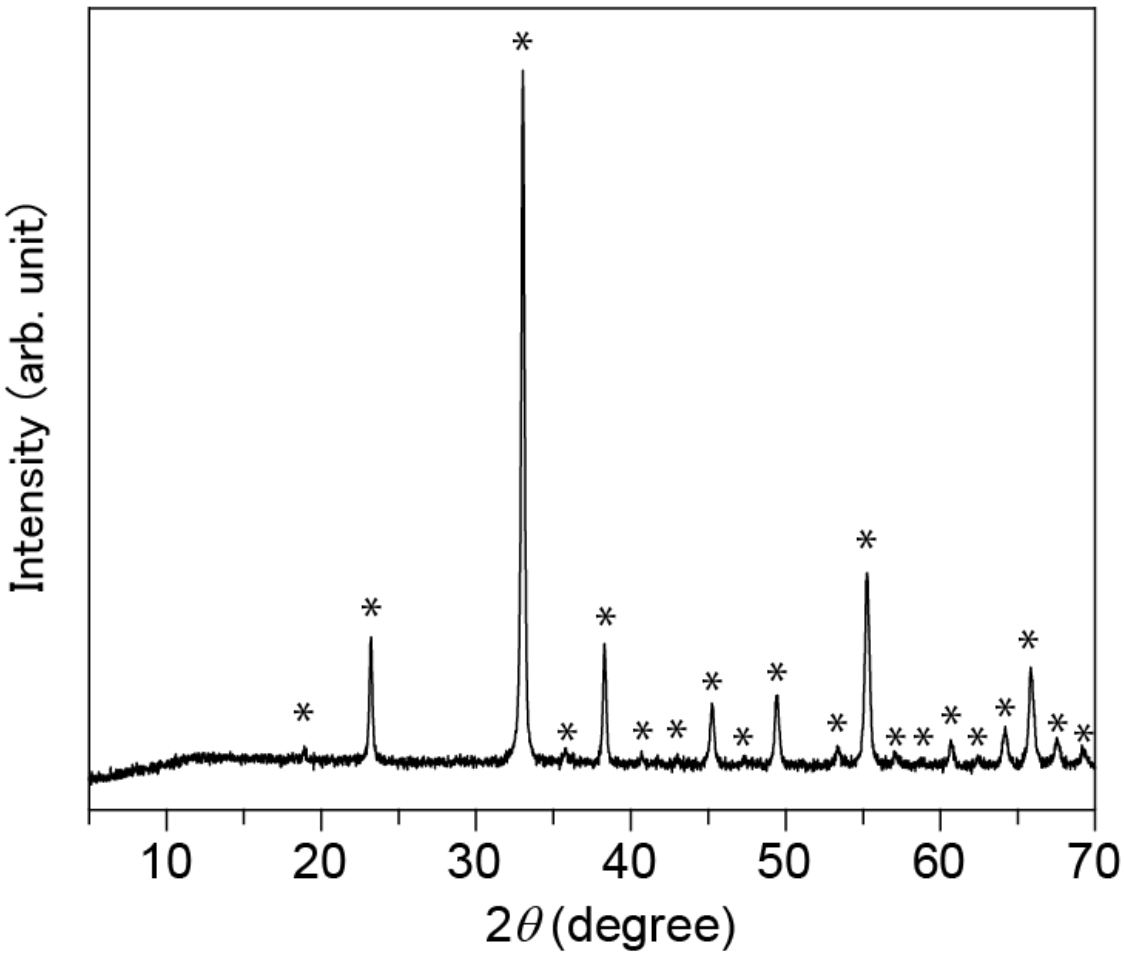

Figure S3. XRD pattern of the C4/MnO_2 after the TG-DTA measurement. All of the XRD peaks are identified as α-Mn_2O_3.

Table S1. The time dependence of pH for r = 2.0 and 4.0.

Reaction time (min.)	pH (r = 2.0)	pH (r = 4.0)
0	12.05 (4)	12.25 (4)
1	7.98 (3)	10.91 (3)
5	7.89 (3)	10.89 (3)
10	7.78 (3)	10.85 (3)
15	7.69 (4)	10.86 (4)
30	7.53 (3)	10.85 (3)
60	7.33 (4)	10.79 (3)
120	7.29 (3)	10.77 (3)
360	7.08 (4)	10.63 (2)

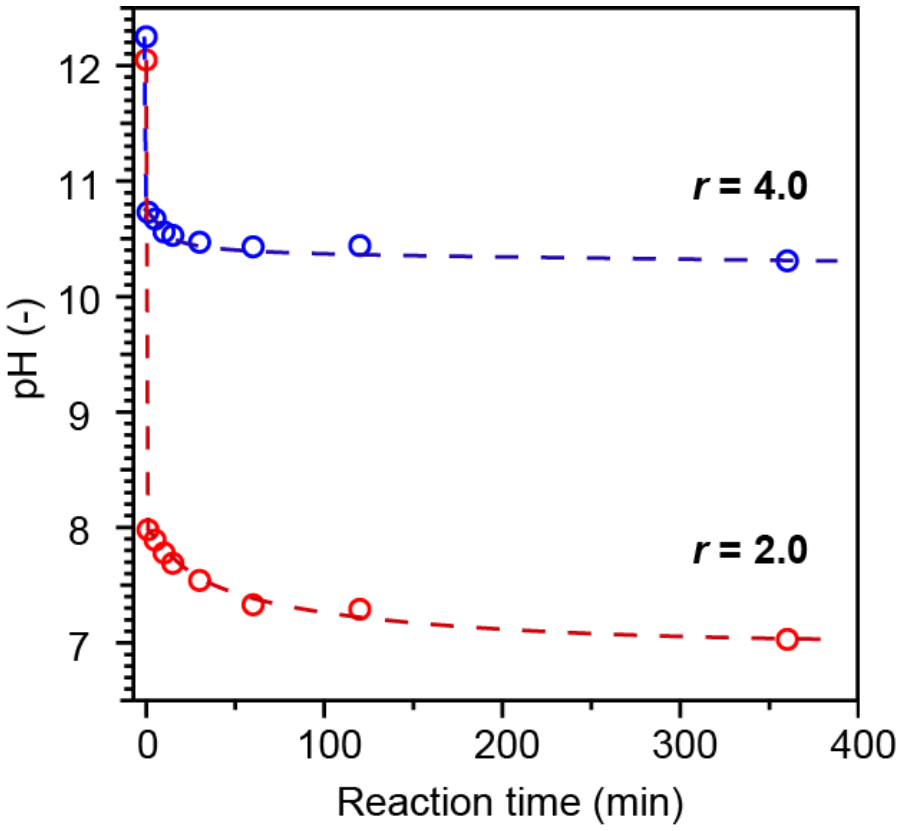

Figure S4. The variation of pH for r = 4.0 (blue) and r = 2.0 (red). Errors are within the markers.

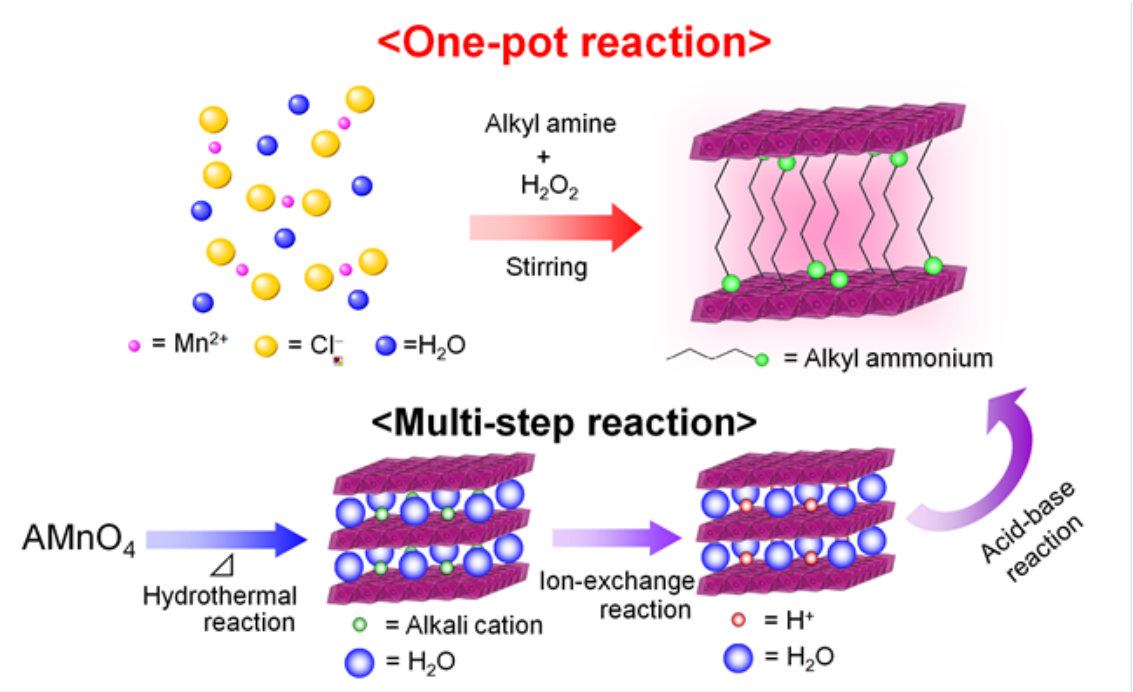

Figure S5. Schematic figure emphasizing the difference between the conventional multi-step and our single-step approaches to obtain layered *n*-alkyl ammonium/MnO_2 hybrids.