Influence of additives on low-temperature hydrothermal synthesis of UO_{2+x} and ThO_2 : Supporting information

1 XRD of UO_{2+x} prepared via hydrothermal synthesis

Figures S1 and S2 display the XRD patterns of UO_{2+x} samples prepared through the hydrothermal syntheses using cyclohexanecarboxaldehyde and propionaldehyde as additives, respectively.



Figure S1: XRD patterns of samples prepared under various temperatures with the addition of cyclohexanecarboxaldehyde.

All the measured samples were revealed to have the fluorite structure without impurities. As shown by the observed pattern for U-B2-9, even the low temperature of 60°C can produce UO_{2+x} with an additive of propional dehyde. The peak width exhibits a clear reaction-temperature dependence; it increases with decreasing the temperature, indicating that an average crystallite size becomes smaller in the samples synthesized at lower temperature. This means that a higher temperature is required for crystal growth in the hydrothermal reactions.



Figure S2: XRD patterns of samples prepared under various temperatures with the addition of propionaldehyde.

2 Rietveld analyses on UO_{2+x} and ThO_2

The typical Rietveld analysis of the XRD pattern is displayed in Fig. S3, along with residuals of the fit (bottom of the figure). In the fittings, UO_2 with the fluorite structure was assumed as the structure model.



Figure S3: Rietveld analysis of the XRD pattern of sample U-B2-6.

Figure S4 shows a typical result of the Rietveld analysis of the XRD pattern of the product obtained from the hydrothermal reaction of Th. As in the case of U, the analysis assumes the fluorite structure.



Figure S4: Rietveldt analysis of the XRD pattern observed for sample Th-A1-2.

3 Reaction-temperature dependence of particle size

Figure S5 shows a typical example of particle sizes plotted as functions of reaction temperatures, for the sample U-B2 series prepared with PA as additive. The data plotted here are the average values of diameters of about 80 particles in the SEM image.



Figure S5: Temperature dependence of particle sizes (samples U-B2-2 to U-B2-7).

4 TGA of products of UO_{2+x} prepared via hydrothermal reactions

TGA curves measured for samples U-B2 and U-B4 series are shown in Figs. S6 and S7.



Figure S6: Thermogravimetric analysis of samples prepared at various temperatures under the addition of propionaldehyde. The bar corresponds to a weight loss of 20% from the initial sample weight.



Figure S7: Thermogravimetric analysis of samples U-B4 series, which were prepared at various temperatures under the addition of Cyclohexanecarboxaldehyde. The bar corresponds to a weight loss of 5% from the initial sample weight.