Supporting Information

The in situ transformation of co-product formaldehyde in the reversible hydrolysis of 1,3-dixoane to get 1,3-propanediol efficiently

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Experimental section

Preparation of Eu$_2$O$_3$. The europium(III) hydroxide sample was prepared by a hydrothermal method. Briefly, 5.14 g of Eu(NO$_3$)$_3$·6H$_2$O was dissolved in 100 mL of Millipore-purified water (18 mΩ· cm), and the solution was adjusted to pH 11.0 by the addition of NH$_4$OH (3.4 M) under magnetic stirring at room temperature. The resulting gel mixture was stirred for 30min and then the white precipate was washed with pure water, dried in an oven at 110 °C overnight. Eu$_2$O$_3$ was obtained by calcinated at 500 °C for 4 h in air.

Preparation of Eu(OH)$_3$-NR. The europium(III) hydroxide sample was prepared by a hydrothermal method. Briefly, 5.14 g of Eu(NO$_3$)$_3$·6H$_2$O was dissolved in 100 mL of Millipore-purified water (18 mΩ· cm), and the solution was adjusted to pH 11.0 by the addition of NH$_4$OH (3.4 M) under magnetic stirring at room temperature. The resulting gel mixture was stirred for 30min and then put it into an autoclave, sealed and then placed in a pre-heated red oven at 180°C for 24 h. The white precipate was washed with pure water, dried in an oven at 110 °C overnight.

Preparation of other metal hydroxides. Various hydroxides were prepared by a precipitation method. For La(OH)$_3$ and Pr(OH)$_3$, a certain amount of Lanthanum nitrate or Praseodymium nitrate was dissolved in 100 mL of Millipore-purified water. Aqueous ammonia was added drop-

wise to the above solutions with stirring. Consequently, the mixture was stirred for 2 h. Then the mixture was filtered and dried at 60 °C. For $Co(OH)_2$, $Ni(OH)_2$, $Cu(OH)_2$ and $Zn(OH)_2$, a certain amount of corresponding metal nitrates was dissolved in 100 mL of Millipore-purified water. Aqueous ammonia was added drop-wise to the above solutions with stirring. The molar ratio of ammonia to added metal was about 2. The resulting gel mixture was washed with water, dried at 60 °C for 12 h. $Mg(OH)_2$ was purchased from Aladdin Chemicals, and were used without further purification.

Hydrolysis of 1, 3-dioxane. Typically, 1, 3-dioxane (1.5 mmol), catalyst (0.1 g), water (1.0 mL) and a magnetic stir bar were added into a Teflon-lined autoclave reactor. The reactor was then sealed and placed in a pre-heated red copper mantle at desired temperature. The reaction was continued for a desired time and was terminated by naturally cooling before opening the reactor for sampling for analysis. The mixing rate is about 600 rpm. After the reaction was completed, the catalyst was filtered out, washed with deionized water then ethanol for three times respectively and drying at 110°C overnight prior to further use in recycling experiment. Products were detected by gas chromatography-mass spectrometry (Agilent7890A/5975C-GC-MS) equipped with a HP-5MS column (30 m in length, 0.25 mm-in. diameter). Conversion and yield were determined by normalizing the integrated peak area.

In the reusable experiment, the used solid $Eu(OH)_3$ was collected by centrifugation after reaction for 6 h. Then it was washed for three times with water, dried in an oven at 60 °C for 12 h, and used in the next cycle.
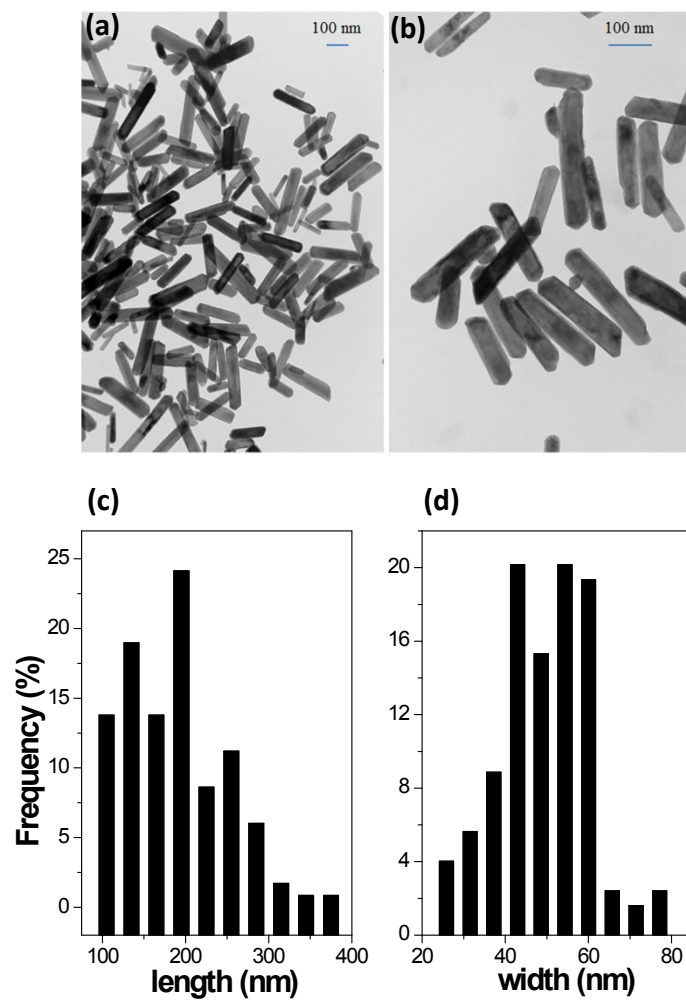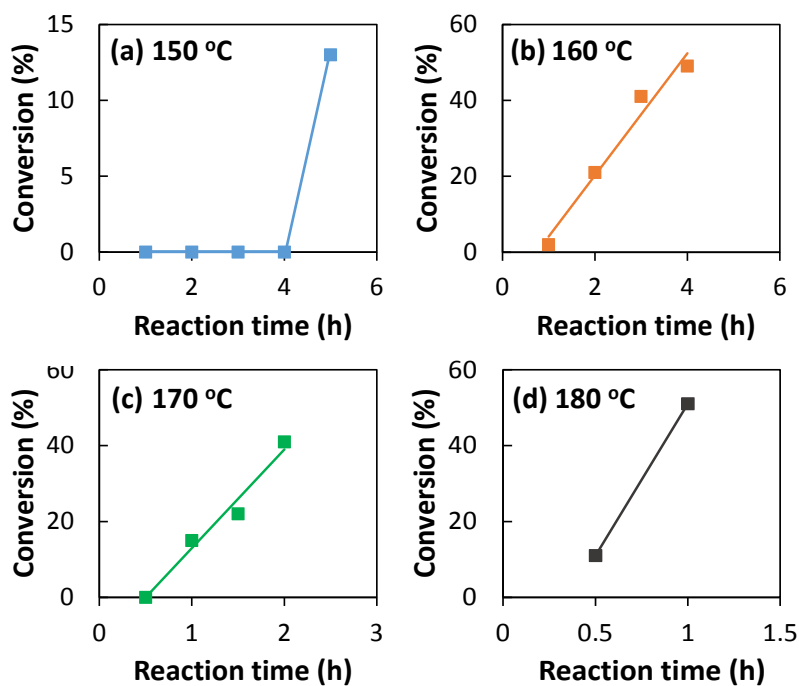
Figure S1. (a) and (b) TEM of Eu(OH)$_3$-NR, (c) The lengths distribution of Eu(OH)$_3$-NR, (d) The widths distribution of Eu(OH)$_3$-NR

Figure S2. The induction period for 1,3-dixoane hydrolysis to 1,3-propanediol in the presence of Eu(OH)$_3$-NR when reaction was conducted at different temperatures ranging from 150 °C to 180 °C. (e) The induction periods and reaction rates at various temperatures obtained from (a) ~ (d).
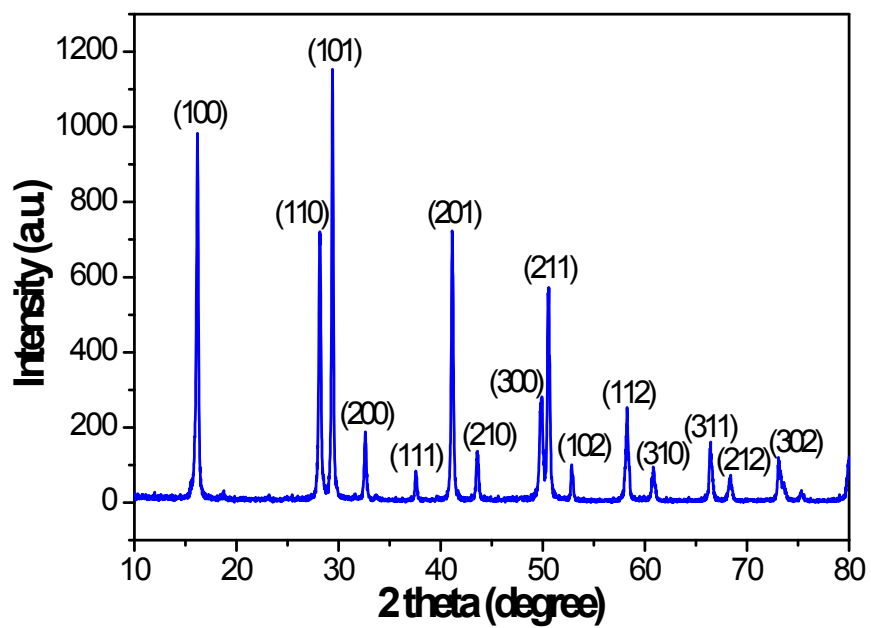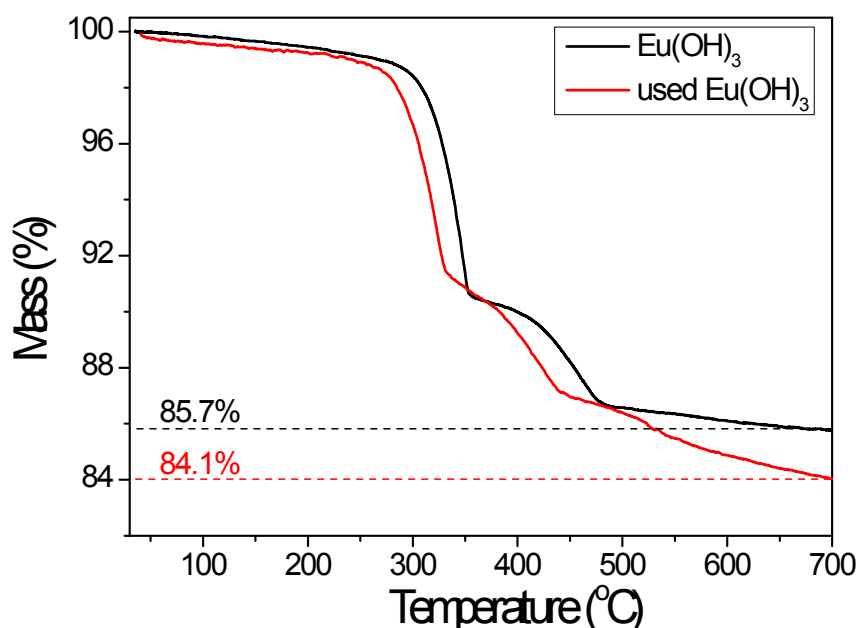
Figure S3. XRD patterns of used Eu(OH)$_3$-NR.

Fig. S4. TG results of fresh Eu(OH)$_3$ and used Eu(OH)$_3$.

TG results of fresh Eu(OH)$_3$ show that the weight loss in the temperature range of 30~700 °C mainly involves two steps, which could be assigned to the transformation of Eu(OH)$_3$ to EuOOH (30~350 °C) and the dehydration of EuOOH to Eu$_2$O$_3$ (350~700 °C), respectively. The weight loss in all is about 14.3%. The TG curve of used Eu(OH)$_3$ shows similar tendency as fresh Eu(OH)$_3$. There is also a two-step weight loss. However, the weight loss in all is 15.9%, which is higher than fresh Eu(OH)$_3$. Combining the results of IR, TG and XRD, we concluded that the extra 1.6 % weight loss is attributed to the removal of organic species on the surface of Eu(OH)$_3$, probably the formate species.
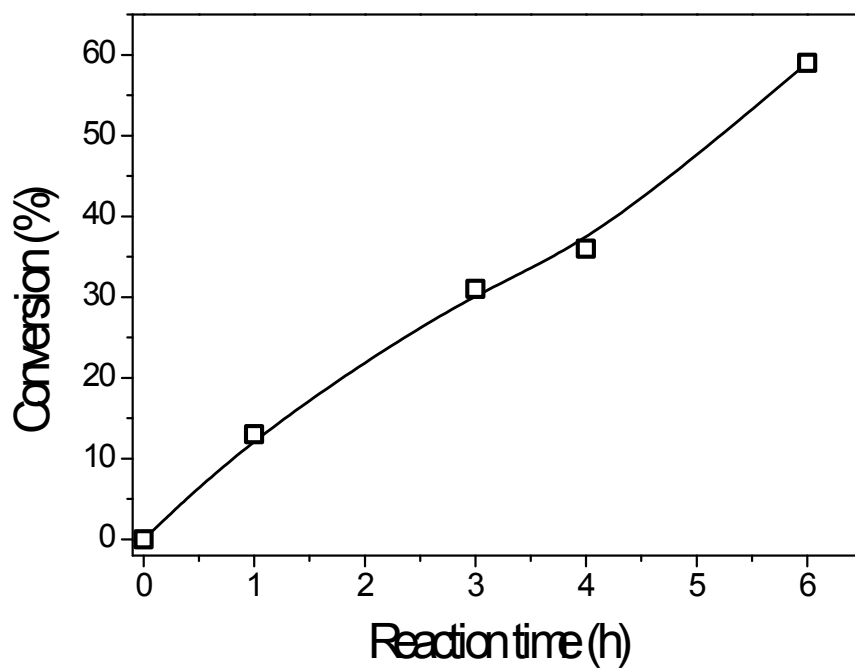
Fig. S5. The hydrolysis of 1,3-dioxane carried out in the presence of

HCOOH. Reaction conditions: Eu(OH)$_3$ 0.1 g, 1,3-dioxane 1.5 mmol,
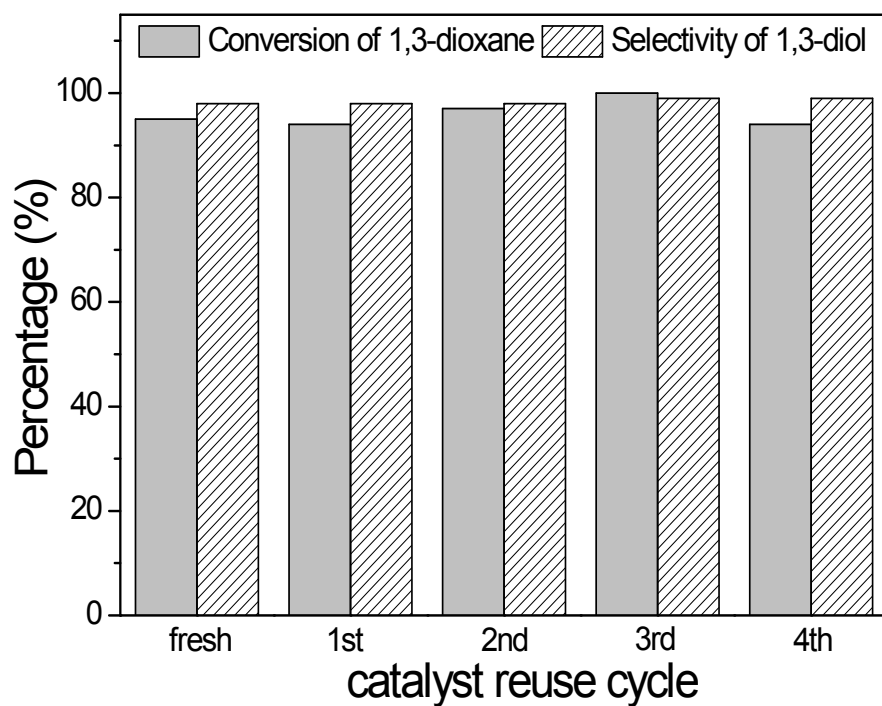
HCOOH 15 mol%, H$_2$O 1mL, 180 ^{o}C.

Fig. S6. Reusability of Eu (OH)₃-NR in the hydrolysis of 1,3-dioxane to 1,3-propanediol. Reaction conditions: catalyst 0.1 g, 1,3-dioxane 1.5 mmol, water 1 mL, 180 ℃, 6 h.
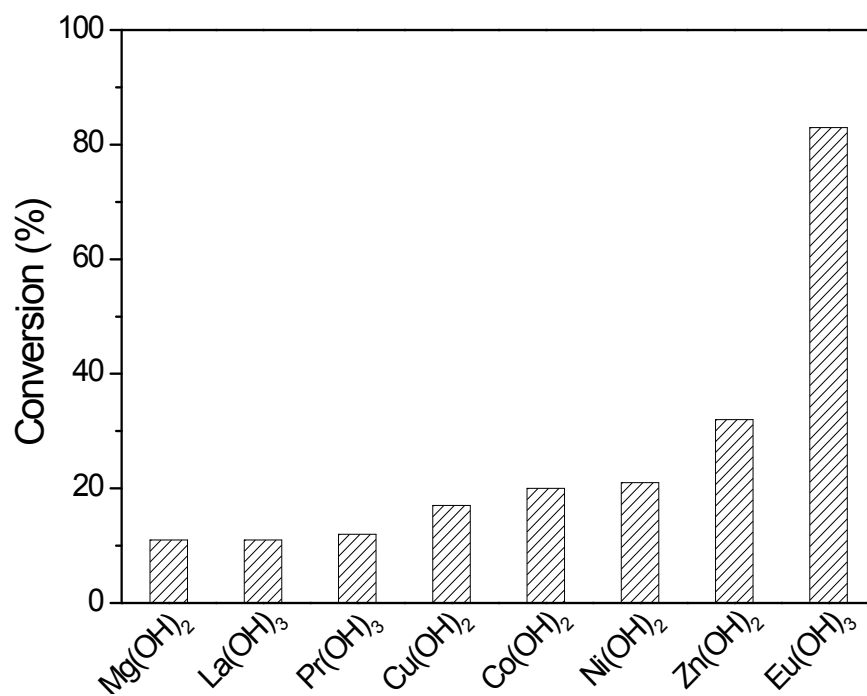
Fig. S7. The hydrolysis of 1,3-dioxane carried out in the presence of various hydroxides. Reaction conditions: catalyst 0.1 g, 1,3-dioxane 1.5 mmol, H_2O 1mL, 180 °C, 3 h.

Table S1. The hydrolysis of different substituted 1,3-dioxanes over this catalytic system.

Substrate	Time / h	Conversion / %	Selectivity / %
	48	97	99
	9	94	99

Reaction conditions: Eu(OH)$_3$ 0.1 g, substituted 1,3-dioxane 1.5 mmol, water 1 mL, 180 °C.