Supporting Information

In situ observation of a mechanically induced self-sustaining reaction for synthesis of silver

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In situ ball mill apparatus

Figure S1 shows the arms and jar holders constructed on the Retsch MM400 mill. The arm consists of five components. The four components were made of aluminum alloy. The other component was a L-shaped connector made of stainless steel. The C-clamp was used as a jar holder.

The start and stop buttons of the modified Retsch MM400 were remotely pressed by servomotors in Fig. S2. The servomotors were connected to a reconfigurable I/O (RIO) device, National Instruments myRIO. The RIO device was connected via USB to PC outside the experimental hutch. The servomotors were controlled using a LabVIEW program. The holders were fixed on an aluminium alloy plate attached to the mill.

3D-printed milling jar

The schematic design of jar is shown in Fig. S4. The jar consists of body and cap. The inner diameters (ID) of jar were 6, 8, 10 and 12 mm. The thickness of jar wall was 0.75 mm, which was as small as possible for three-dimensional (3D) printing to minimize scattering from a jar. The inside length of jar was 36 mm except for the edge hemisphere parts. The internal volumes were 1.13, 2.08, 3.35 and 4.98 cm^3 for the jars of ID: 6, 8, 10, and 12 mm, respectively. The outside total length of jar was 56 mm. The edge outer diameters were 10, 12, 14 and 16 mm for the jars of ID: 6, 8, 10 and 12 mm, respectively. The jars were produced using polylactic acid (PLA), acrylonitrile butadiene styrene (ABS),[1] and polycarbonate (PC) by a 3D printer, Tiertime UP mini 2.

Rietveld refinements of the *in situ* diffraction data

Rietveld refinements of the *in situ* synchrotron radiation (SR) powder X-ray diffraction (PXRD) data were performed with our developed multi-distance method using synchrotron

powder (SP) program.[2] The analyzed 2θ ranges were from 11° to 40°, from 8.5° to 40°, and from 11° to 40° for the *in situ* diffraction data for ball milling of aluminum (Al) and nickel (Ni) powder and for mechanochemical reduction of silver chloride (AgCl) with Al, respectively. The background was described by 12th-order polynomial. In the refinements, two to four sample-to-detector distances L_i were determined. The diffraction peaks from the milling jar were described by Pearson VII functions. The lattice parameters of the metals were determined to be fixed as the values of 4.0494 Å and 3.5243 Å determined using the unmilled samples[3] for Al and Ni, respectively, for all the *in situ* data. Atomic displacement parameters were set as an identical value for all the sample-to-detector distances. The structure of Al, Ni and silver (Ag) consists of the atom at the 4*a* site (0, 0, 0) with the space group of $Fm\bar{3}m$. The crystal structure of AgCl consists of Ag atom at the 4*a* site (0, 0, 0) and Cl atom at the 4*b* site (0.5, 0.5, 0.5) with the space group of $Fm\bar{3}m$. For $AgCl_3 \cdot 6H_2O$ and SiO_2 of the balls, the reported structural parameters[4,5] were used.

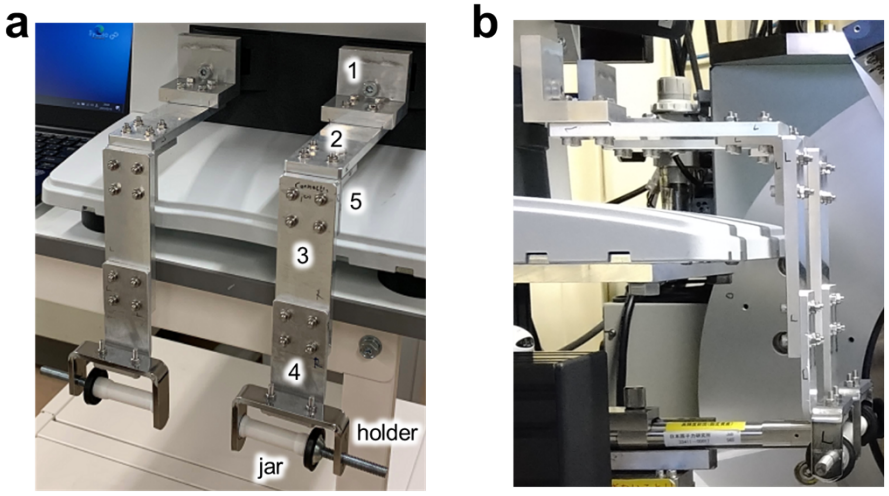

Figure S1. Arm of ball mill for *in situ* SR-PXRD. (a) The arm consists of five components indicated by 1 to 5. The components 1−4 are made of aluminum alloy. The component 5 is a L-shaped connector made of stainless steel. (b) Side view. The stainless steel spacers are inserted between the holder and the component 4 to optimize the height of jar.

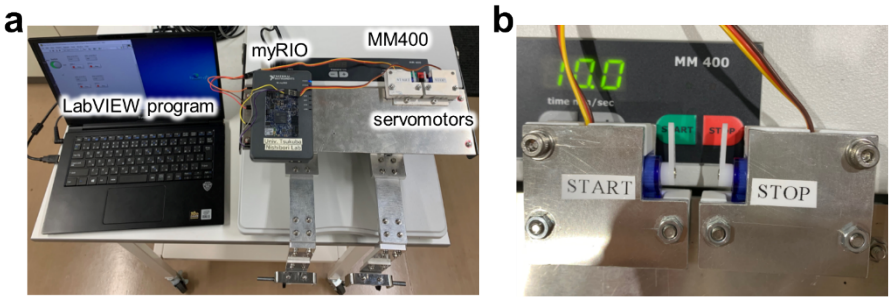

Figure S2. System for ball mill operation. (a) The system consists of servomotors, National Instruments myRIO, and PC. The servomotors are controlled using a LabVIEW program. (b) The arms of servomotors press the start and stop buttons of Retsch MM400.

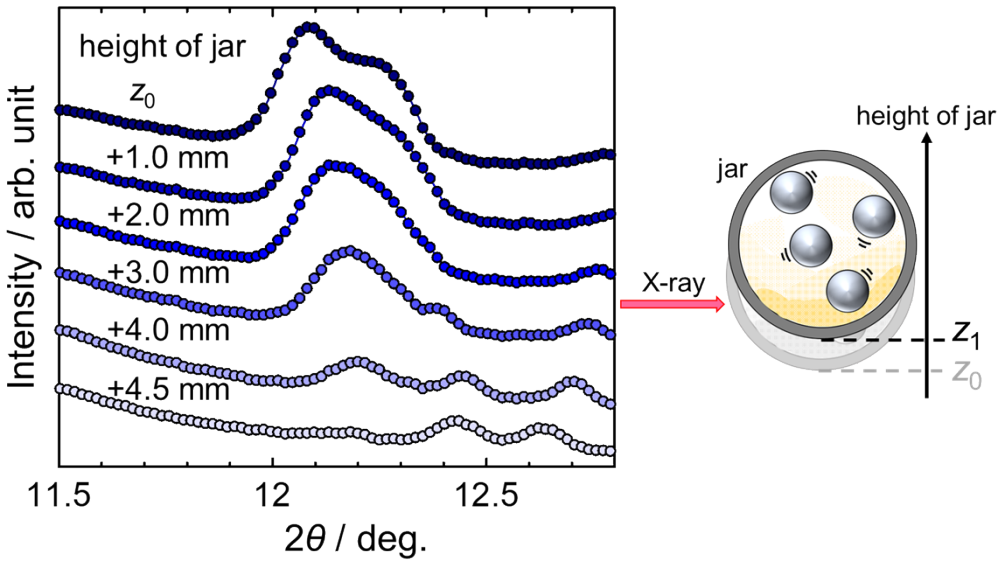

Figure S3. Jar height dependence of intensity of SiO_2 110 reflection from agate milling balls. The inset represents the height of jar. The *in situ* synchrotron X-ray diffraction data were measured for 60 s with the wavelength of 0.7 Å. The ball milling was operated with 20 Hz using the PLA jar with ID of 12 mm and four balls with a diameter of 3 mm.

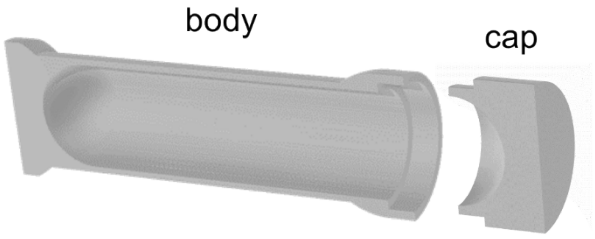

Figure S4. Cross-sectional drawing of jar with an inner diameter of 12 mm.

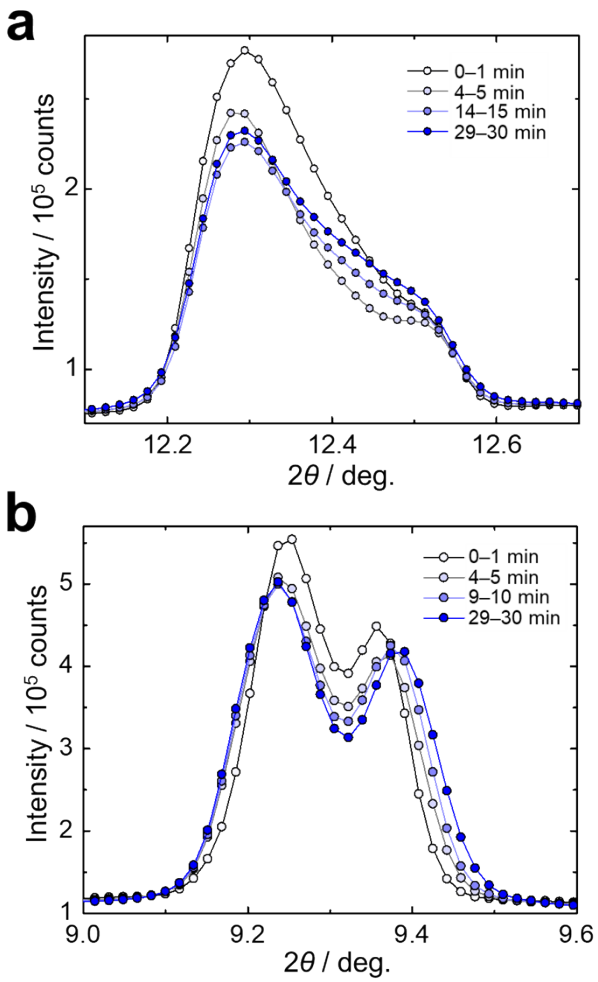

Figure S5. Powder diffraction profiles of 111 reflection of (a) Al and (b) Ni during ball milling.

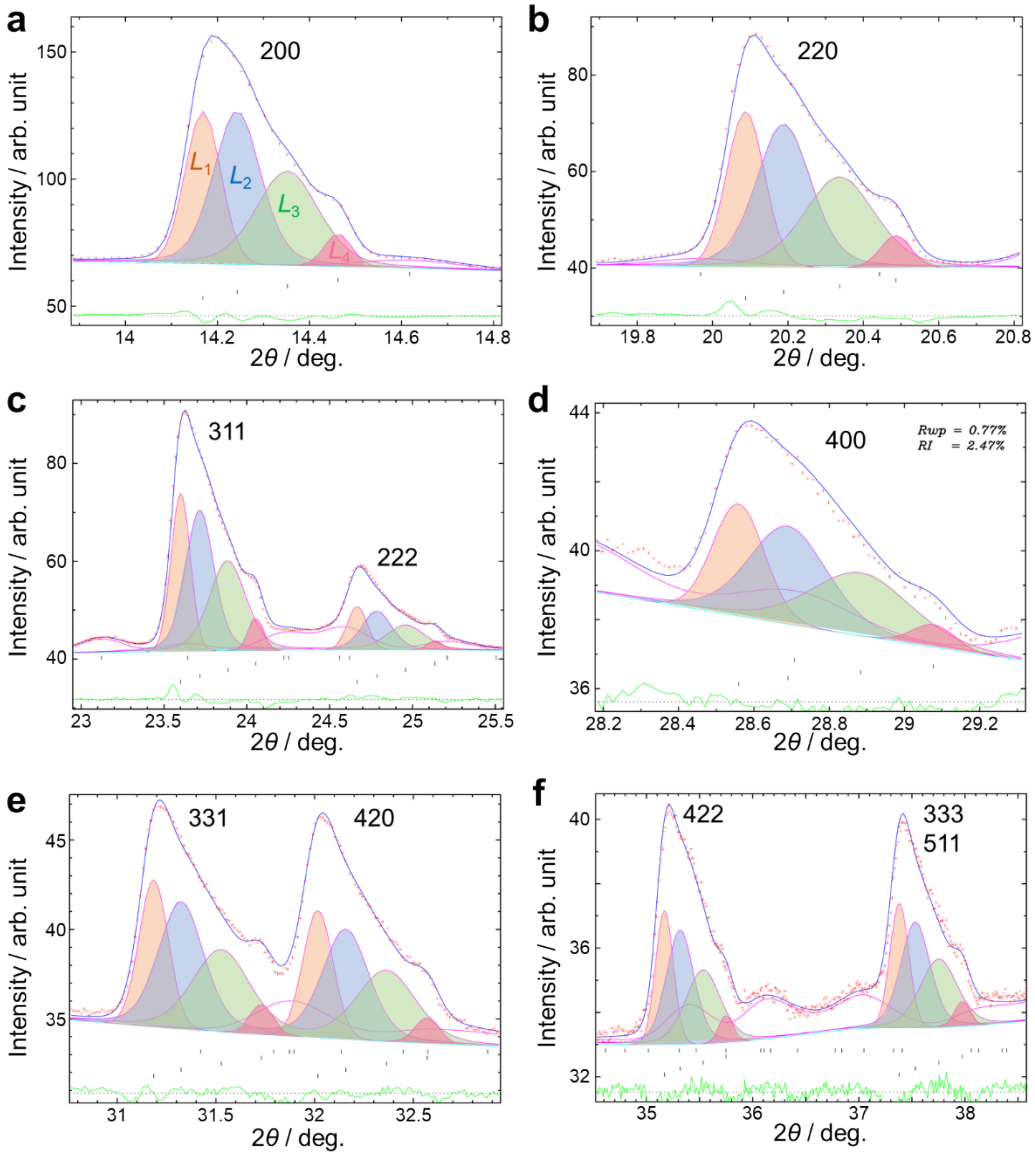

Figure S6. Fitting result of Rietveld refinement for SR-PXRD data of Al powder during ball milling. (a) 200, (b) 220, (c) 311 and 222, (d) 400, (e) 311 and 420, and (f) 422, 333 and 511 reflections of Al.

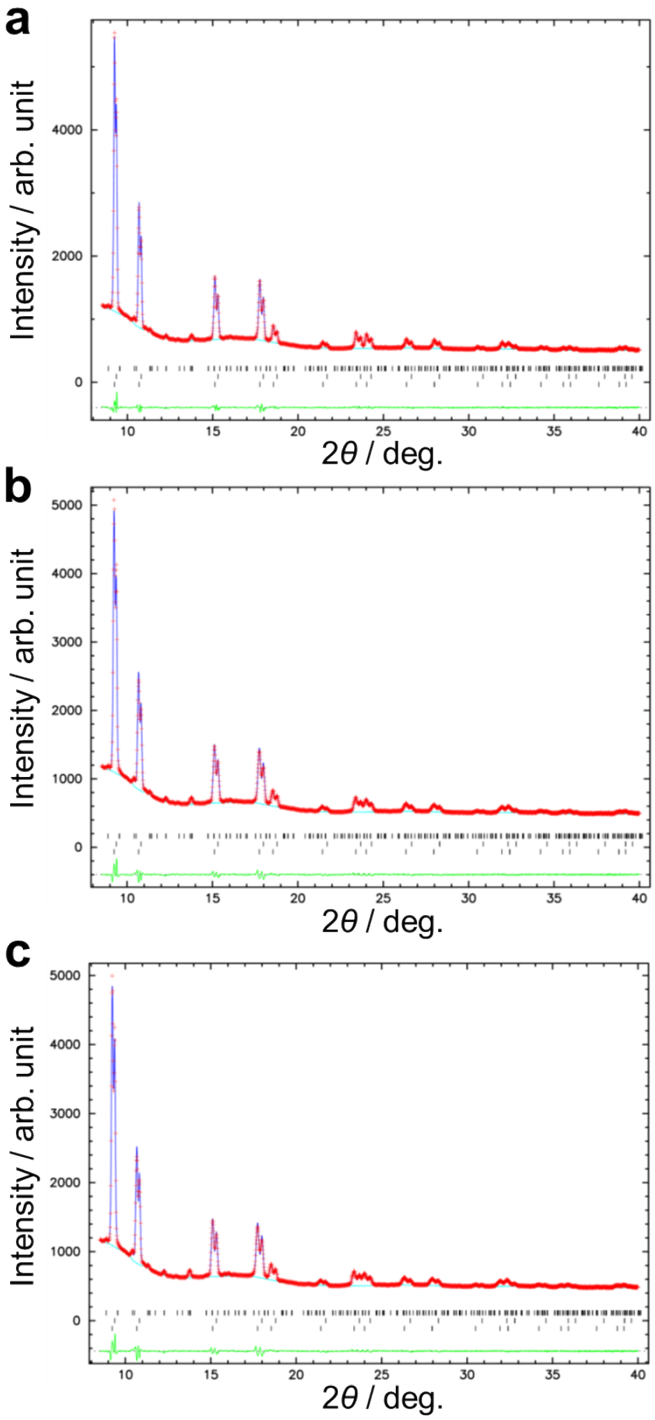

Figure S7. Fitting result of Rietveld refinements for SR-PXRD data of Ni powder during ball milling. (a) 0−1 min. R_{wp} = 1.18% and R_I = 2.07%. (b) 4−5 min. R_{wp} = 1.41% and R_I = 2.51%. (c) 9−10 mim. R_{wp} = 1.56% and R_I = 2.66%.

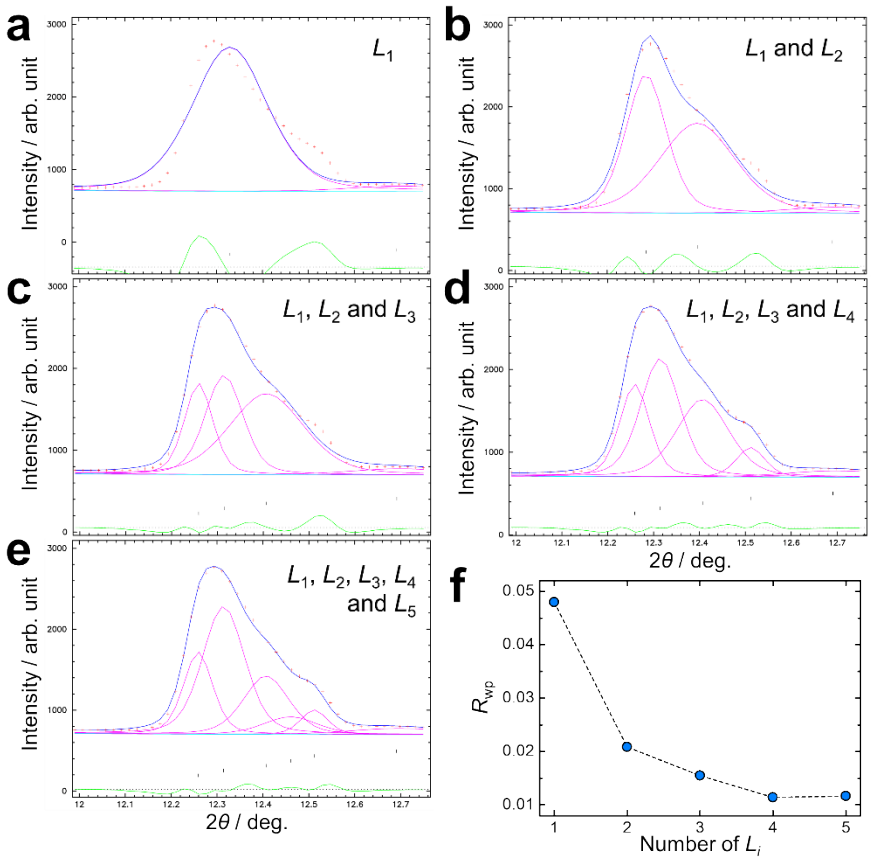

Figure S8. Rietveld refinements using the multi-distance method for the *in situ* SR-PXRD data of Al with changing number of sample-to-detector distances L_i. (a-e) Fitting results for the 111 reflection of Al using (a) one, (b) two, (c) three, (d) four and (e) five L_i. (f) Change of R_{wp} by number of L_i.

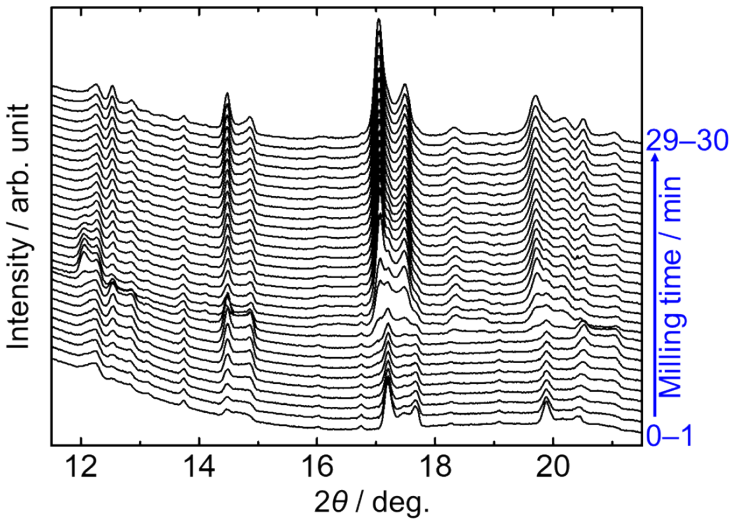

Figure S9. *In situ* SR-PXRD pattern during the mechanochemical reduction. The representative 2θ was transformed from the FPD pixel number using L = 323.3 mm and x_0 = −164.

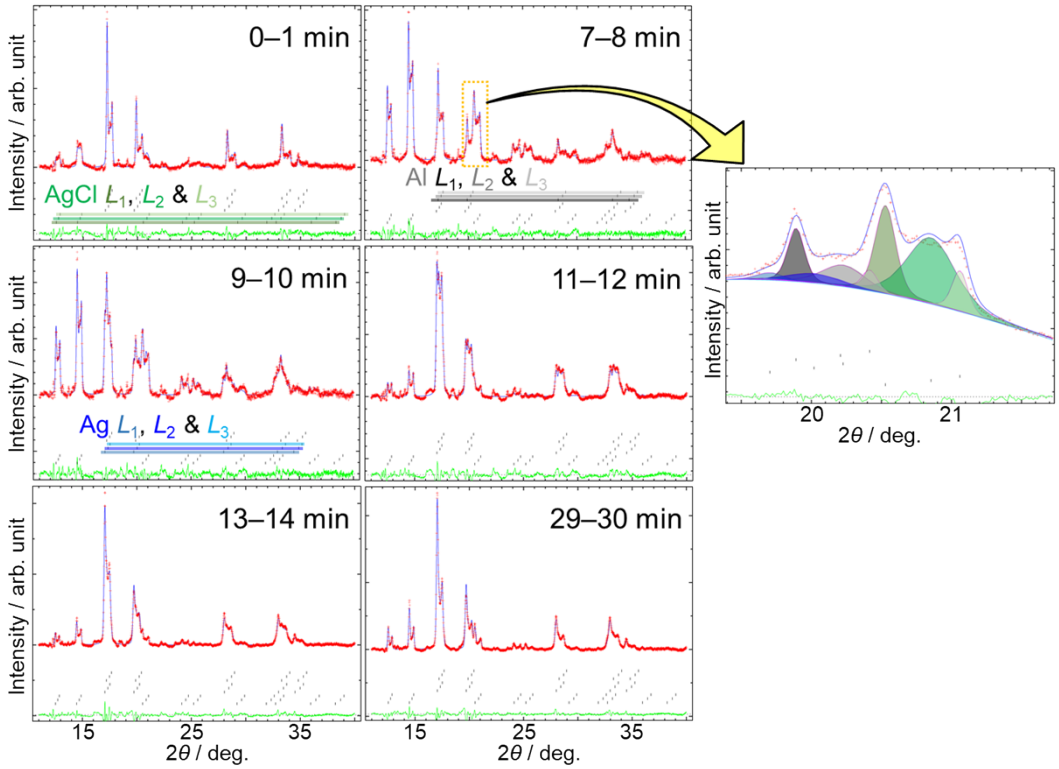

Figure S10. Fitting results of Rietveld refinement for the *in situ* SR-PXRD data of the mechanochemical reduction. The background is subtracted except the inset.

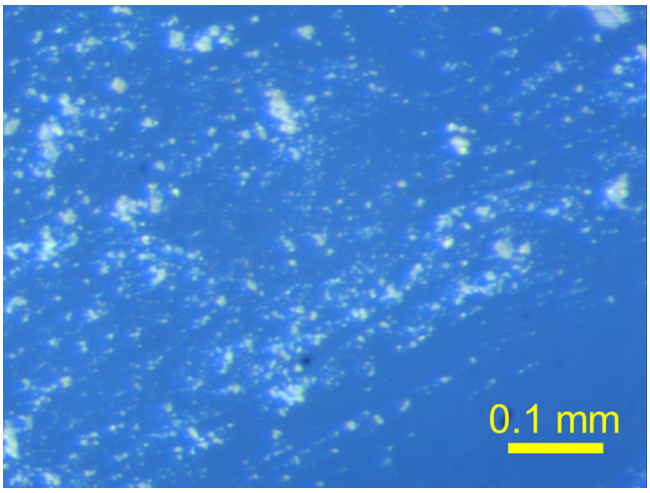

Figure S11. Optical microscope picture for product of the mechanochemical reduction. The powder adhering to jar walls was viewed on a glass plate.

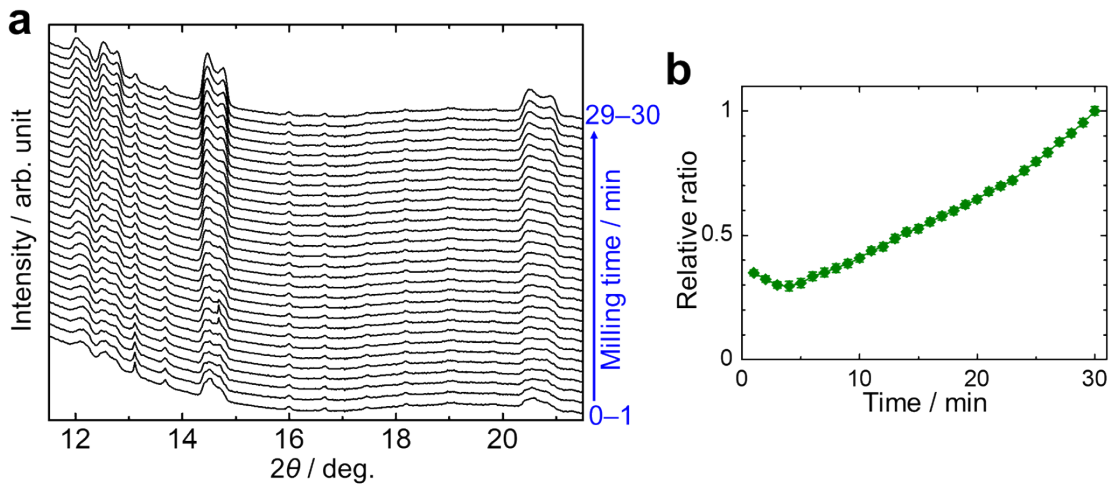

Figure S12. *In situ* SR-PXRD for ball milling of only AgCl. (a) Diffraction pattern. (b) Normalized scale factor of Rietveld refinement using the multi-distance method. The representative 2θ was transformed from the FPD pixel number using $L = 323.3$ mm and $x_0 = -164$.

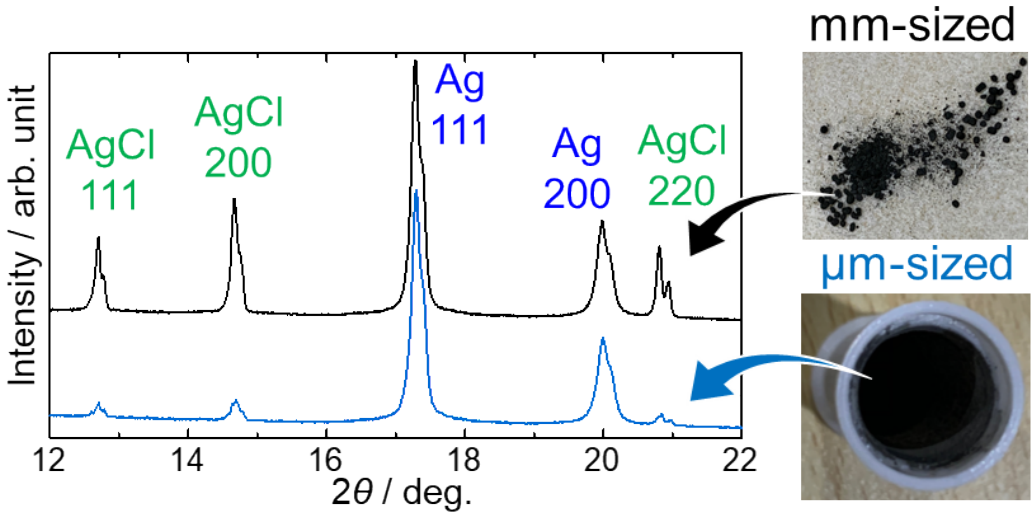

Figure S13. PXRD of the product for millimeter-sized aggregates and micrometer-sized particles.

Supporting References

[1] N. Tumanov, V. Ban, A. Poulain and Y. Filinchuk, *J. Appl. Crystallogr.* 2017, **50**, 994.

[2] E. Nishibori, E. Sunaoshi, A. Yoshida, S. Aoyagi, K. Kato, M. Takata and M. Sakata, *Acta Crystallogr., A: Found. Crystallogr.* 2007, **63**, 43.

[3] T. Sasaki, H. Kasai and E. Nishibori, *Sci. Rep.* 2018, **8**, 11964.

[4] D. R. Buchanan and P. M. A. Harris, *Acta Crystallogr., B* 1968, **24**, 954.

[5] H. d'Amour, W. Denner and H. Schulz, *Acta Crystallogr. B: Struct. Sci.* 1979, **35**, 550.