

Supporting Information

Exploring Mass Transfer as a Parameter in Mechanochemical Processes

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Experimental

Materials

Nicotinamide ($\geq 99.5\%$) and salicylic acid ($\geq 99.0\%$) were both obtained as crystalline powders from Sigma-Aldrich and used without further purification. Red phosphorus (99.7% purity) was obtained as a powder from Merck and used without further purification or processing. TiO_2 (99.0%) was obtained as a powder from Riedel-de Haën and used without further purification. High-purity synthetic grade water was obtained from Milli-Q® Advantage A10 Water Purification System. Phosphate-buffer (PB, 10 mmol, ThermoFischer Scientific). All other chemicals and reagents were supplied from different commercial providers and used without further purification unless otherwise stated.

Methods

General

All PBM experiments were performed using “Pulverisette 6” mono mill from FRITSCH GmbH. The tests were performed using an 80 mL stainless-steel ball-mill chamber (hardened stainless steel - 1.4125, ISO/EN/DIN code: X105CrMo17 with pressure-sealed lid a Teflon O-ring) and stainless-steel medium (hardened stainless steel - 1.4125, ISO/EN/DIN code: X105CrMo17) also supplied by FRITSCH GmbH. Before each experiment, the chamber and milling media were cleaned using water and/or isopropanol and dried with paper towels. The BPR ratios for the different experiments were selected based on preliminary studies. All experiments utilized an arbitrary 25:1 BPR, except for the red to black phosphorus allotropic conversion reaction and the abrasion test. The allotropic conversion of red to black phosphorus is more energy demanding than the co-crystallization of nicotinamide and salicylic acid, so a higher BPR was used for this process. Additionally, all experiments were performed at an rpm of 600 unless stated otherwise.

Production of MB

MB was produced by modifying the stainless-steel ball-mill medium provided by FRITSCH GmbH (hardened stainless steel - 1.4125, ISO/EN/DIN code: X105CrMo17). The balls were 10 mm in diameter. The carved corrugations were done

using Weiler Matador Type W lathe (WEILER Werkzeugmaschinen GmbH). The balls were fitted onto a 10 mm ball-holder to carve the first line on the side using hardened steel (triangular edge). The balls were then placed onto a smaller ball-holder (the same diameter as the carved line) and were held by the first small carved line to then carve the middle line and the other side line. The balls were rotated 90° along the dimension of the carved lines and the same procedure was repeated to carve the 3 other lines. The balls were stabilized while turning using a metal cone fitted in the machine. The carved corrugations were 1 mm deep. After the machining process, MB can be conditioned by milling in an inert powder (i.e. sodium chloride) for 15 min at 600 rpm, under any suitable loading and BPR, to smoothen the sharp edges (see SI 1 for weight and abrasion analysis of the milling media).

The design of MB was devised after consideration of the following points. Generally, the design of the milling ball (MB) must be both easy and fast to machine, allowing for scalability reproducibility. It should maintain an overall spherical structure to preserve the general motion of the milling medium inside the planetary ball-mill's chamber. This spherical design helps mitigate abrasion during milling, thereby enhancing the longevity of the MB and reducing metal contamination compared to designs with protruding points and edges. The MB must also feature corrugations to enable better penetration into the samples, effectively homogenizing them and ensuring higher product quality and consistency. However, the corrugations should not be too deep to avoid material sticking in the ridges and to prevent deformation of the MB's overall shape during milling. Additionally, the corrugations should not be too shallow, as this would cause the ridges to flatten during the milling process.

Conversion of Red to Black Phosphorus

For the monitored conversion of red to black phosphorus, red phosphorus (1 g, ≥97.0%, Merck) was placed in the 80 mL stainless-steel ball-mill chamber together with either a combination of MB and NB (1:4) or only NB (60:1 BPR) in a glovebox under argon atmosphere ($O_2 < 0.6$ ppm, 9-10 mbar) and sealed before transferring it to the ball-mill. The ball-mill operated at 600 rpm for a duration that ranged from 1 to 4 hours depending on the intent of the experiment. For monitored experiments, samples were extracted in an inert glovebox at different time points. After every hour,

the ball-mill was paused for cooling of the machine and reversal of the flywheel rotation. For the low-BPR conversion of red to black phosphorus, red phosphorus (1 g, $\geq 97.0\%$, Merck) was placed in the 80 mL stainless-steel ball-mill chamber together with either a NB or MB (6 units, 25:1 BPR) in a glovebox under argon atmosphere ($O_2 < 0.6$ ppm, 9-10 mbar) and sealed before transferring it to the ball-mill. The ball-mill operated at 600 rpm for a duration of 4 hours. After every hour, the ball-mill was paused for cooling of the machine and reversal of the flywheel rotation.

Co-crystallization of Nicotinamide and Salicylic Acid

Nicotinamide (488 mg, $\geq 99.5\%$, Sigma-Aldrich) and salicylic acid (552 mg, $\geq 99.0\%$, Sigma-Aldrich) were placed in the 80 mL stainless-steel ball-mill chamber together with either NB or MB (6 units, 25:1 BPR) and sealed before transferring it to the ball-mill. The ball-mill operated at 600 rpm for a duration of 10 to 60 min depending on the intent of the experiment.

Size Reduction of TiO_2

TiO_2 (1 g, 99.0%, Riedel-de Haën) was placed in the 80 mL stainless-steel ball-mill chamber together with either NB or MB (6 units) and sealed before transferring it to the ball-mill. The ball-mill operated at 600 rpm for a duration of 5 to 15 min depending on the intent of the experiment.

Thermal Assessment of MB using FLIR

NB or MB (6 units, 25:0 BPR) was placed in the 80 mL stainless-steel ball-mill chamber and sealed before transferring it to the ball-mill. The ball-mill operated at 200-600 rpm for a duration of 10 to 60 min depending on the intent of the experiment. A FLIR camera (FLIR, 0-350 °C, Model EX, FLIR® Systems) fixed onto a tripod was placed in a set position pointing towards a designated place for the ball-mill chamber for consistent capturing of the thermal images.

Abrasion Test of MB

3 units of unconditioned MB were placed in an 80 mL stainless-steel ball-mill chamber together with 1 g of sodium chloride ($\sim 10:1$ BPR) and sealed before transferring it to the ball-mill. The ball-mill was operated at 600 rpm for 15 min before extracting the conditioned MB and weighing them. The conditioned MB were transferred back to the same chamber and the ball-mill was operated for another 8 hours before extracting the MB milling medium again and weighing them.

Raman Spectroscopy

Raman spectroscopy was used for the measurement of powder samples as it is a facile technique that can provide thorough analysis of a material by measurement of spatially

resolved Raman maps. Raman spectroscopy measurements were done using a Horiba Xplora spectrometer equipped with an x/y piezo stage. Laser excitation for all measurements was set at 532 nm which was delivered through a 100x objective (Nikon®). To avoid thermal heating and/or degradation of the samples, the laser power was filtered to 1 % of the intensity for all measurements. All spectra were measured with 1 second accumulation time. Samples were deposited on silicon dioxide/silicon wafers (1 cm x 1 cm).

Statistical Raman spectroscopy (SRS) was conducted by measurement of Raman maps over sample regions deposited on the Si or SiO₂/Si substrates. The average spectra were calculated from the maps and the Si-only spectra were filtered out. Accumulation time for each spectrum was set to 1 second. Substrate movement for the mapping was done using the motorized x/y piezo stage.

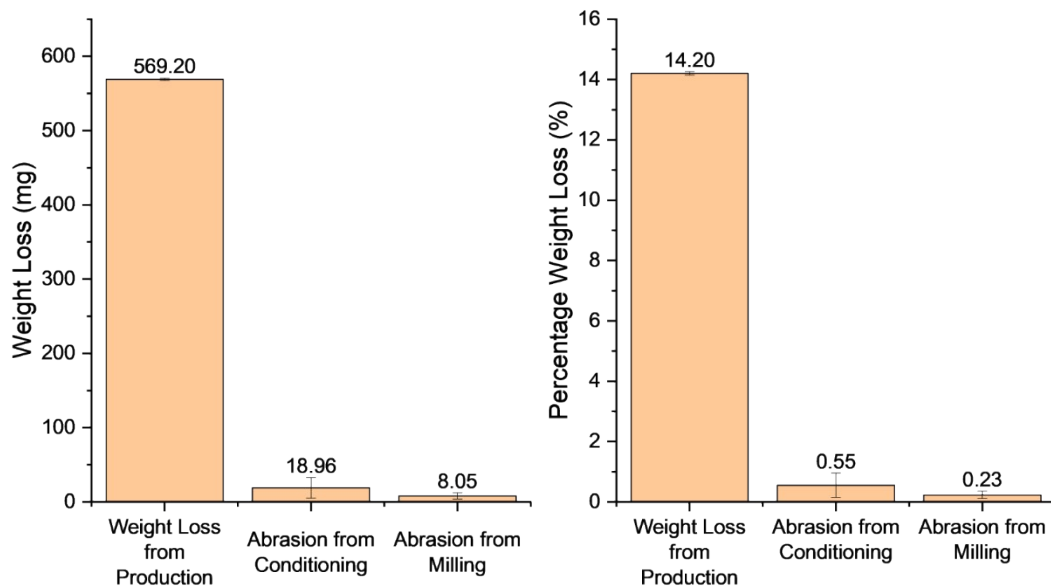
DLS

DLS data was measured using the Malvern Zetasizer Nano device (Brookhaven Instruments Corp.) at room temperature (25 °C). The TiO₂ sample concentrations were set at 1 mg mL⁻¹ concentration in 1% citric acid aqueous solutions (w/w). For every sample, three measurement runs were recorded, and the average of the results was used.

Statistical Analysis

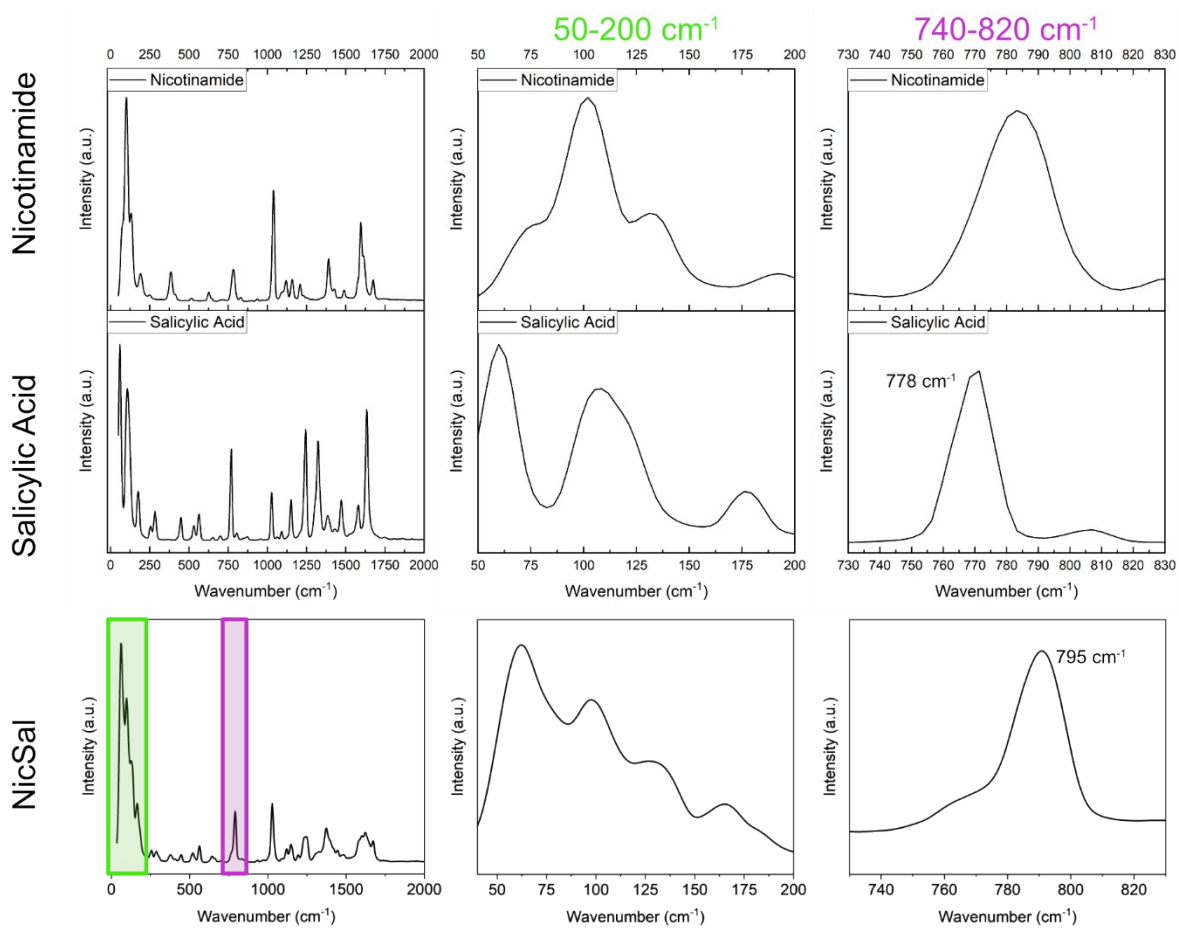
All statistical data represent the mean ±SD. Sample sizes for all experiments were $n = 3$. Statistical Raman spectroscopy was used for all Raman analyses.

Characterization

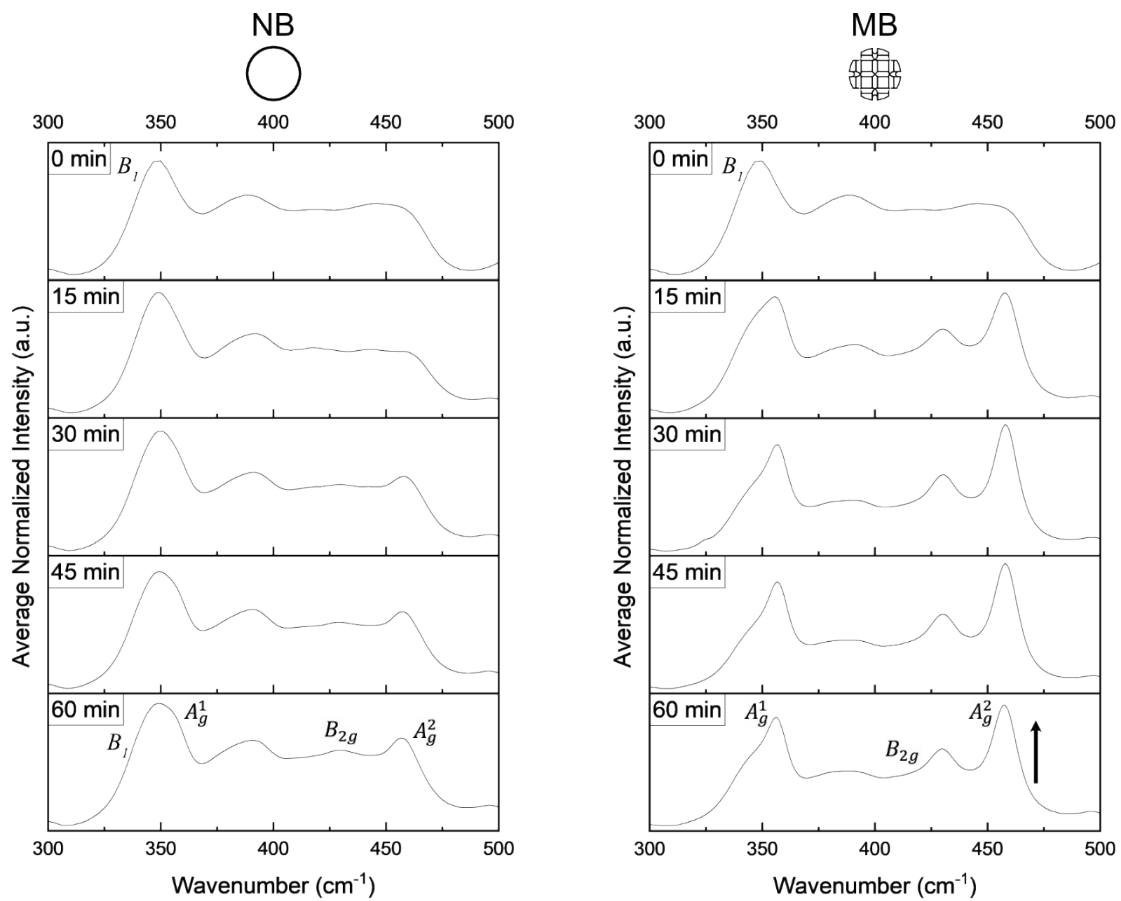


SI 1: Weight loss of MB from production and abrasion from conditioning and milling (3 units after 8 hours of milling at 600 rpm).

The MB milling medium can be conditioned directly after production to remove the sharp edges from the balls, which slightly reduces their weight. The rate of abrasion of MB (hardness: ~60 Hardness Rockwell C, density: 7.7 kg/dm³) from milling 1 g of sodium chloride at 600 rpm and a BPR of 10:1 is ~1.01 mg hr⁻¹.



SI 2: Raman spectra of nicotineamide, salicylic acid, and NicSal.



SI 3: Spatially resolved Raman spectra of monitored red to black phosphorus conversions using either only NB or ¼ MB-to-NB mixture (60:1 BPR).

