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Electronic Supplementary Information

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Alumina-mediated mechanochemical method for simultaneously degrading perfluorooctanoic acid and synthesizing a polyfluoroalkene†

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Experimental

Isolation of 1H-1-PFHp as the major product

To isolate the major product 1H-1-PFHp, the MC conversion experiment of PFOA was conducted with an increased scale by several independent runs. In each run, 1.18 g PFOA was treated with 7.22 g alumina at a ball-to-powders weight ratio of 50. The reaction was ended at 3 h of ball milling. After the reaction was ended, 20 mL diethyl ether was slowly injected into the milling pot, and the extracted dispersion was cleaned by a filtration treatment. Then, the collected clean solution was transferred into a 25 mL round-bottomed flask, and the flask was placed on a water bath under the magnetic stirring. The water bath was slowly heated to 45 °C, and the vapor temperature was controlled at (34.5 ± 0.5) °C, which was very close to the boil point of diethyl ether. The diethyl ether was recovered in the distillate fraction on a Vigreux column (30 × 1.5 cm), and the organic product was collected in the residual fraction (RF). The distillation process was stopped when the vapor temperature started cooling down. Finally, the isolation yield was calculated from the mass of the product. In addition, the components in both distillates and residual fraction were analysed to accesses the purity of 1H-1-PFHp. Prior to GC-FID analysis, both DF and RF were diluted with acetone by 100 times. The relative distribution of 1H-1-PFHp to diethyl ether was achieved based on the relative correction factors (f_{m}).

The applicability of the isolation method was accessed by using nanofluoro-1-hexene (PFBE) as a reference compound. When a 6 mL mixture of PFBE and diethyl ether (1:5, V/V; 1.4:3.6, m/m) was subjected to an atmospheric distillation (35 °C), it was obtained 1.30 g residual fraction containing PFBE (purity, 92%) and 3.28 g distillate containing diethyl ether (purity, 97%). This indicated the above isolation steps can be applied to simultaneously separate 1H-1-PFHp and recover the solvents.

Quantification of organic products

The quantification of 1H-1-PFHp was analyzed by GC measurements with fluorobenzene as the internal standard. GC analyses were conducted on a gas chromatography-flame ionization detector system (GC-FID, 7890B, Agilent, USA) equipped with an Rtx-502.2 column (60 m × 0.32 mm × 1.8 µm, Restek, USA). The injector and FID temperatures were set at 200 and 260 °C, respectively. The oven temperature program started at 25 °C for 2 min and was increased at 10 °C/min up to 180 °C and maintained at 180 °C for 5 min.

Because pure authentic standards of the products were not commercially available, quantification of the products was achieved by comparing their response signals to those of an internal standard (fluorobenzene, FB) with simulated relative correction factors ($f_{\mathrm{m,pre}}$). The amount of each product was calculated by the following equation (eq. S1),

$$m_{\mathrm{product}} = \frac{f_{\mathrm{m,pre}} \times m_{\mathrm{FB}} \times A_{\mathrm{product}}}{\alpha \times A_{\mathrm{FB}}} \qquad \text{S1}$$

where m_{product} and m_{FB} are the masses of the substances, A_{product} and A_{FB} are the integrals of the FID responses of the substances, and α is the correction constant of the real f_{m} toward the predicted $f_{\mathrm{m,pre}}$, respectively.

The $f_{\mathrm{m,pre}}$ value of each product relative to fluorobenzene was calculated by the following equation (eq. S2) as reported by Chaintreau et al.[1, 2]

$$f_{\mathrm{m,pre}} = \frac{M_{\mathrm{product}}(-61.5+88.8n_{\mathrm{C(FB)}}+18.7n_{\mathrm{H(FB)}}-20.2n_{\mathrm{F(FB)}}+127n_{\mathrm{benz(FB)}})}{M_{\mathrm{FB}}(-61.5+88.8n_{\mathrm{C(product)}}+18.7n_{\mathrm{H(product)}}-20.2n_{\mathrm{F(product)}})} \qquad \text{S2}$$

where n_{C}, n_{H}, n_{F} and n_{benz} are the number of carbon, hydrogen, fluorine and benzene rings, respectively and M_{product} and M_{FB} are the molecular weights of the substances.

To verify the simulated $f_{\mathrm{m,pre}}$, the homologous compounds PFBE and PFO, which have similar perfluorinated carbon chains, were chosen as the model substances. We compared the relative correction factors of PFBE (or PFO) to FB, toluene (TOL) and *n*-hexane (Hex) as internal standards between the simulated value and measured values.

The standard solutions of both analytes (PFBE and PFO) and internal standards (FB, TOL and Hex) were made by accurately weighing approximately 0.0500 g of the compound into a 10-mL volumetric flask, and then diluting the sample with acetone to volume. A series of solutions were prepared by dissolving various volumes of PFBE (or PFO) and certain volumes of FB, TOL and Hex standard solutions, and the total volume of each solution was fixed at 1.5 mL. Then, the mixtures of PFBE (or PFO) with the three internal standards were analyzed using GC-FID under the abovementioned conditions. For example, the experimental $f_{\mathrm{m,exp}}$ values of PFBE to FB were calculated by the following equation (eq. S3):

$$f_{\mathrm{m,exp}} = \frac{m_{\mathrm{PFBE}} \times A_{\mathrm{FB}}}{m_{\mathrm{FB}} \times A_{\mathrm{PFBE}}} \qquad \text{S3}$$

where m_{PFBE} and m_{FB} are the masses of the substances and A_{PFBE} and A_{FB} are the integrals of the FID responses of the substances, respectively.

Results and discussion

Method validation of the GC-FID quantification of organic products

For a mixture of PFBE, FB, TOL and Hex, there were differences of less than 10% between the predicted f_{m} and the measured $f_{\mathrm{m,exp}}$ values; the exception to this was the predicted $f_{\mathrm{m,pre}}$ of PFBE to the other three internal standards (Table S1). The $f_{\mathrm{m,pre}}$ value of PFBE was approximately 1.65 times more than the corresponding measured $f_{\mathrm{m,exp}}$ value. This indicated that $f_{\mathrm{m,exp}}$ values of the perfluorinated derivatives had deviated from their predicted $f_{\mathrm{m,pre}}$ values. A shift in the $f_{\mathrm{m,exp}}$ of the perfluorinated derivatives was also observed for a mixture of PFO, FB, TOL and Hex (Table S2). Interestingly, the predicted $f_{\mathrm{m,pre}}$ of PFO to the other three internal standards was also 1.65 times more than the measured $f_{\mathrm{m,exp}}$. Thus, the real f_{m} for the perfluorinated derivatives can be correlated from the predicted $f_{\mathrm{m,pre}}$ by the following equation (eq. S4):

$$f_{\mathrm{m}} = \frac{f_{\mathrm{m,pre}}}{1.65} \tag{S4}$$

That is, by combining a correlation factor of 1.65, the predicted $f_{\mathrm{m,pre}}$ value can be used to quantify the amount of polyfluoroalkenes. To evaluate the accuracy of the estimation method by using the predicted $f_{\mathrm{m,pre}}$ value, we investigated the quantification of PFBE by using fluorobenzene as the internal standard. A series of samples were prepared by dissolving various amounts of PFBE and certain amounts of fluorobenzene in acetone, and then analyzing those samples with GC-FID under the abovementioned conditions. Based on Eq. S3, the $f_{\mathrm{m,pre}}$ of PFBE was calculated to be 4.98. By using Eq. S5, the mass of PFBE could be calculated, and the results are shown in Table S3. Recoveries ranged from 93.9% to 108.4% with relative standard deviations of less than 5%. These results indicated that the analysis method was high reproducible and confirmed the method performed acceptably. Thus, the method can be used to quantify the polyfluoroalkene content by using the predicted $f_{\mathrm{m,pre}}$ (eq. S3) and a correlation factor of 1.65.

Similarly, the f_{m} of 1H-PFHp to diethyl ether was calculated to be 3.6, which was employed to accesses the relative distribution of components in both distillates and residual fraction.

Table S1. Analysis of PFBE using FB, MB and Hex as internal standards and the compiled relative response factors

	$f_{\mathrm{m,exp}}$	$f_{\mathrm{m,pre}}$	$f_{m,pre}/f_{m,exp}$
PFBE/FB	2.96	4.98	1.68
	3.04		1.64
PFBE/TOL	3.72	6.47	1.74
	3.65		1.77
PFBE/Hex	3.62	6.06	1.67
	3.69		1.64
Hex/TOL	0.97	1.07	1.10
	1.03		1.04
Hex/FB	0.86	0.82	0.95
	0.94		0.88
FB/TOL	1.20	1.30	1.08
	1.13		1.12

Table S2. Analysis of PFO using FB, MB and Hex as internal standards and the compiled relative response factors

	$f_{\mathrm{m,exp}}$	$f_{\mathrm{m,pre}}$	$f_{m,pre}/f_{m,exp}$
PFO/FB	6.36	10.73	1.69
	6.97		1.54
PFO/TOL	9.10	13.94	1.53
	8.86		1.57
PFO/Hex	7.77	13.06	1.68
	7.96		1.64
Hex/TOL	1.18	1.07	0.91
	1.13		0.99
Hex/FB	1.09	0.82	0.85
	0.75		0.82
FB/TOL	1.26	1.30	1.03
	1.56		0.83

Table S3. Analysis of PFBE using FB as an internal standard and the determination results

Sample	$m_{PFBE,add}$ /μg	A_{PFBE} / a.u.	m_{FB} /μg	A_{FB} / a.u.	$m_{PFBE,det}$ /μg	*Recovery* /%
1	1587	62530.2	8678.5	1022514.6	1602.8	101.0
		60413.5		951446.6	1664.2	104.9
		58689.6		904814.9	1700.0	107.1
2	3174	120929.3	7147	854749.4	3053.7	96.2
		121244.6		854934.3	3061.0	96.4
		119607.8		823469.7	3135.0	98.8
3	5290	176289.1	5105	531977.4	5109.0	96.6
		194415.4		589461.7	5084.9	96.1
		189683.5		559454.2	5227.2	98.8
4	6348	208731.6	4084	376967.8	6829.3	107.6
		214852.5		385200.7	6879.3	108.4
		220607.4		427328.5	6367.2	100.3
5	1521	54237.4	9299	1014223.4	1501.8	101.0
		45366.9		920118.8	1384.6	98.7
		52801.6		992104.5	1494.6	91.0
6	3042	124252.9	7658	939391	3059.0	98.3
		131479.2		946070.8	3214.1	100.6
		117559.9		913167.4	2977.4	105.7
7	5070	206299.1	5470	675014.6	5048.7	97.9
		208853.1		675014.6	5111.2	99.6
		185576.4		616177.9	4975.2	100.8
8	6084	231294.4	4376	513607.1	5951.4	98.1
		223195.4		482101.2	6118.3	97.8
		249277		544512.2	6050.1	100.6
9	8112	305606.4	2188	247006.4	8175.4	99.4
		323848.1		260554.4	8212.9	100.8
		345943.4		281285.7	8126.7	101.2
10	8464	230437.1	2042	178802.3	7947.7	93.9
		300477		225166.1	8229.5	97.2
		236946		181338.4	8057.9	95.2
Average recovery /%						99.6
Relative deviation /%						4.0

Defluorination of different substrates by MC process and thermal treatment

Table S4 compared the degradation and defluorination of different fluorinated compounds. In the MC/Al_2O_3 system, the 2-h MC treatment resulted in a high degradation removal (95.9%) of PFOA and a low defluorination efficiency (14.1%). According to eq. S1, the selectivity of the generated F^- ions was calculated and it seemed to be unchanged (13.1 ± 3.2%). When the MC/Al_2O_3 system was used to treat the shorter chain perfluorinated carboxylic acids, all the added substrates were degraded after 2-h MC treatment, but it also gave a low defluorination efficiency and selectivity (< 25%). This indicated a controlled partial defluorination of perfluorinated carboxylic acids in the MC/Al_2O_3 system. Perfluorooctane, which has the same C–F framework but lacks the carboxyl group, was subjected to the MC/Al_2O_3 treatment. Both the conversion and defluorination of perfluorooctane were negligible in the MC/alumina system. Thus, the acid-base reaction between the COOH group of perfluoro acids and the surface OH groups on the alumina is necessary to strongly anchor the perfluoro acids during their MC defluorination reaction.

As is well known, unlike alumina, SiO_2 has an abundance of surface OH groups available but no Lewis acid sites. The defluorination of PFOA was significantly suppressed in MC/SiO_2 system and 2 h of milling only reached 2.9% defluorination and a F^- selectivity of 6.6%. These differences suggested that the Lewis acid sites on the alumina played a critical role in the breakage of the C−F bonds.

In addition, a 30-min heat treatment at 150°C decomposed only 21.9% of the PFOA and showed a very low defluorination rate (1.1%). This implies that a simple combination of alumina and thermal treatment was not efficient in breaking the C−F bonds.

Table S4. Conversion and defluorination of different substrates after a MC conversion and thermal treatment.

Substrate	System	Time (h)	Conv. (%)	F^- ions	
				Y (%)	S (%)
PFOA	MC/Al_2O_3	0.5	39.7	5.1	12.7
		1	60.8	8.6	14.1
		2	95.9	14.1	14.7
	MC/SiO_2	0.5	16.8	2.9	17.3
		2	42.2	2.8	6.6
$C_6F_{13}COOH$	MC/Al_2O_3	1	98.1	15.0	15.3
		2	100	16.1	16.1
C_4F_9COOH	MC/Al_2O_3	1	99.1	22.7	22.9
		2	100	23.2	23.2
C_8F_{18}	MC/Al_2O_3	0.5	2.2	2.9	/
		2	2.8	2.7	/
PFOA	150°C/Al_2O_3	0.5	21.9	1.1	5

Identification and quantification of organic products

The FT-IR spectrum of the products is presented in Figure 1b in the main text. The peaks at 1100~1300 cm^{-1} were assigned to the characteristic absorptions of C−F stretch, and the characteristic bands of C=C and aliphatic C−H stretches were clearly observed at 1676 cm^{-1} and 3011 cm^{-1}, respectively.[3] These bands confirmed that the organic product was a fluorinated aliphatic olefin.

GC-MS and FT-MS were used to further identify the organic product. Figure 1c shows the total ion current (TIC) profile and MS data of the product. The TIC profile indicated that there were two products, but the major product had a retention time of 5.80 min. According to the MS data, the major product showed fragments similar to those of the precursor with m/z= 69.36 (CF_3), 118.97 (CF_3CF_2), 169.18 ($CF_3CF_2CF_2$), 218.79 ($CF_3(CF_2)_2CF_2$), 231.06 ($CF_3(CF_2)_3C$) and 281.06 ($CF_3(CF_2)_4C$). From the FT-MS analysis (Figure S1a), the component with m/z=330.93884 in the negative ion mode could be assigned to the $CF_3(CF_2)_4CF{=}CF^-$ fragment (theoretical m/z, 330.97924). Taken together with the FTIR result, the major organic product may be identified as 1H-perfluorohept-1-ene ($CF_3(CF_2)_4CF{=}CFH$).

The molecular structure of the major organic product was further clarified by ^{19}F and ^{13}C NMR spectroscopy. Figure 1d shows the ^{19}F NMR spectrum of the PFOA solution and the spectrum of the extracted organic products generated by PFOA milling with Al_2O_3 for 2 h. For the PFOA solution, the resonance at −82.9 ppm was assigned to the terminal $C(1)F_3$; the resonances for the CF_2 units in the backbone ($C(3\text{-}5)F_2$) were in the −122.1 to −123.5 ppm range; the peak at a lower frequency (−126.7 ppm) and the peak at a higher frequency (−119.4 ppm) that that of the main CF_2 peak were attributed to the CF_2 group adjacent to the terminal CF_3 and the CF_2 group next to the carboxylic acid group ($C(7)F_2$ and $C(2)F_2$), respectively.[4] After the 2.5-h MC treatment (i.e., in the case of the extracted organic product), the resonance of the CF_2 group adjacent to the COOH group and one of the backbone CF_2 units at −119.4 and −122.1 ppm had disappeared. Instead, two new peaks at −129.9 and −139.2 ppm were observed, which were attributed to the =CF− and =CFH units, respectively.[5] From the ^{13}C NMR spectrum of the organic product (Figure S1b), five peaks centered in the 105.6 to 118.5 ppm range were observed, and they corresponded to the carbon atoms of $-CF_2CF_2CF_2CF_2CF_3$, respectively, and the peaks at 124.9 and 128.2 ppm were attributed to the carbons of the =CF− and =CFH groups, respectively.[6]

Similarly, according to the MS data (Figure S2), the product with a retention time of 4.78 min showed fragments with m/z of 51.32 (CF_2), 68.81 (CF_3), 130.97 ($CF_2CF{=}CF_2$), 181.21 ($(CF_2)_2CF{=}CF_2$), 230.90 ($(CF_2)_3CF{=}CF_2$) and 331.01 ($CF_3(CF_2)_4CF{=}CF$), which could be assigned to perfluorohept-1-ene ($CF_3(CF_2)_4CF{=}CF_2$). The other product, which had a retention time of 5.04 min, showed fragments with m/z of 51.37 (CF_2), 68.80 (CF_3), 101.01 (CF_2CF_2), 131.03 ($CF_2CF{=}CF_2$), 231.07 ($(CF_2)_3CF{=}CF_2$), and 250.21 ($CF_3(CF_2)_2CF{=}CF_2$), which could be assigned to 1H-perfluoropent-1-ene ($CF_3(CF_2)_2CF{=}CFH$).

Based on the MC conversion of PFOA and the yield of the product, the selectivity of 1H-1-PFHp was calculated from the following equation (eq. S6):

$$\text{Selectivity }\% = \frac{\text{yield of products}}{\text{conversion ratio of PFOA}} \times 100\% \qquad \text{S6}$$

The calculated selectivity is shown in Figure S3. A good correlation was obtained between the yield of 1H-1-PFHp and the conversion of PFOA within 2.5 h of ball milling, and the selectivity of the conversion of PFOA into 1H-1-PFHp was consistently up to 89%.

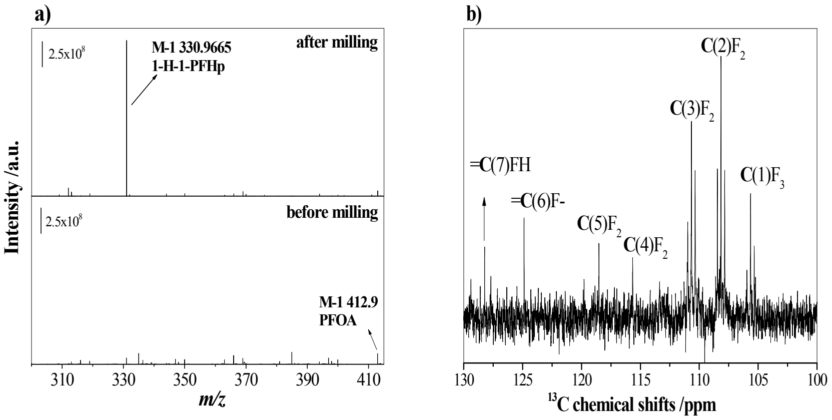

Figure S1. FT-MS spectra (a) and ^{13}C NMR spectrum (b) of the samples extracted during MC conversion of PFOA within 2.5 h; acetone was using as the extraction agent. Prior to NMR measurements, 200 μL extracts was diluted with 500 μL acetone-D_6.

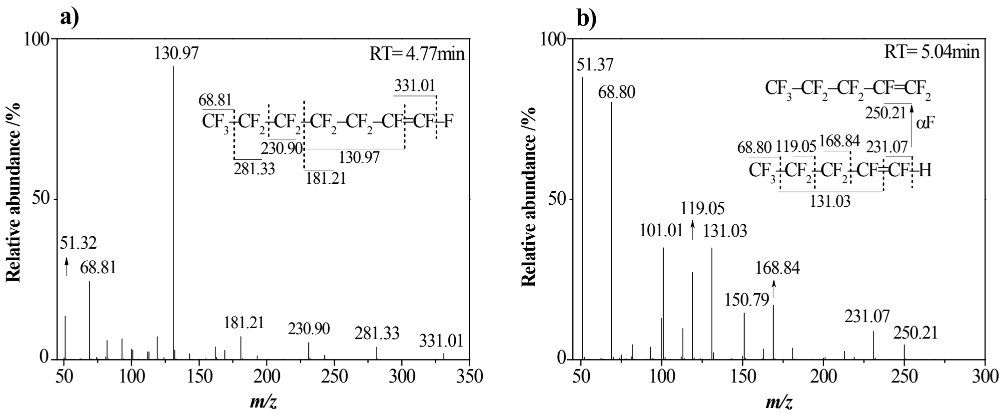

Figure S2. GC/MS profiles of the minority products (a. perfluorohept-1-ene and b. 1H-perfluoropent-1-ene) after 2.5 h of ball milling of PFOA with alumina. Acetone was used as the extraction agent.

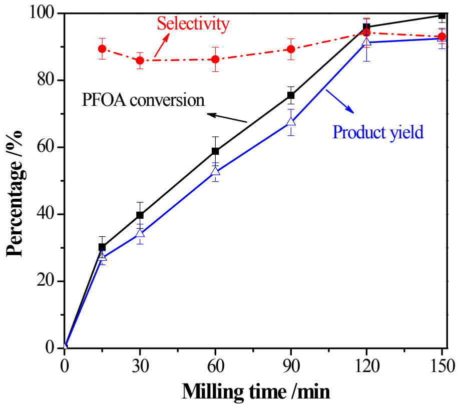

Figure S3. MC conversion of PFOA into 1H-1-PFHp by milling PFOA with alumina.

Possibilities of scale-up on the MC conversion of PFOA into 1H-1-PFHp

The scale-up experiments have been conducted at a higher PFOA/alumina weight ratio (R_w), a larger filling ratio and a lower ball-to-powders weight ratio (m_b/m_p), and the results were shown in Table S5 and Figure S4. At a given R_w value of 16.3% and a filling ratio of milling pot (R_f) at 35%, as the m_b/m_p value was increased from 10 to 100, both the degradation of PFOA and the generation of 1H-1-PFHp was significantly improved in an m_b/m_p range of 10~50, and then reached a platform when the m_b/m_p value was beyond 50. Thus, the m_b/m_p was recommended as 50 in this work unless specified elsewhere. At an m_b/m_p of 50, an increasing in the R_w value from 8.2% to 16.3% did not influence the 2-h conversion of PFOA, but slightly increased both the yield and selectivity of 1H-1-PFHp, due to that at a lower R_w value, excessive alumina increased the defluorination ratio. When the R_w value was further increased from 16.3% to 40.5%, both the degradation of PFOA and the selectivity of 1H-1-PFHp was gradually decreased, but all the added PFOA could be converted with a 1H-1-PFHp selectivity of >80% if prolonging the MC treatment time to 4.5 h. Moreover, when the R_f value was increased from 20% to 60% at a fixed m_b/m_p of 50 and R_w of 16.3%, the MC treatment of PFOA (1.18 g) with alumina (7.22 g) (i.e., 60% of filling ratio) also gave the high yield of 1H-1-PFHp (87.6%, GC yield) within 3 h.

Table S5. Conversion (Conv.) of PFOA into F⁻ and 1H-1-PFHp in the MC/alumina system at a R_f of 35% after 2 h treatment.

R_w (%)[a]	m_b/m_p	PFOA Conv. (%)	F⁻		1H-1-PFHp	
			Y (%)	S (%)	Y (%)	S (%)
16.3	10	25.3	4.5	17.8	8.9	35.2
	25	68.7	9.7	14.1	36.9	53.7
	50	95.9	14.1	14.7	91.3	95.2
	100	98.6	15.6	15.8	92.8	94.1
8.2	50	97.8	17.8	18.2	82.2	84
11.7		98.1	16.1	16.4	88.4	90.1
20.3		85.9	11.7	13.6	75	87.3
24.3		63.2	8.1	12.8	50.7	80.3
40.5		10.3	0.6	5.8	4.0	38.8

[a]: weight ratio of PFOA/Al_2O_3.

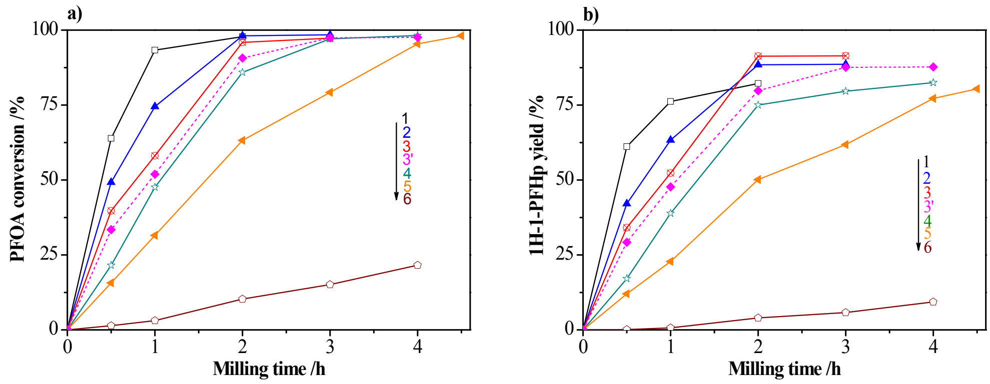

Figure S4. Conversion of PFOA into 1H-1-PFHp in MC/alumina systems at an m_b/m_p of 50 but at different PFOA/Al_2O_3 weight ratios of 8.2 (1), 11.7 (2), 16.3(3, 3’), 20.3 (4), 24.3 (5), and 40.5 (6). The filling ratio of milling pot was 35%, except for the case of (3’) in which it was 60%.

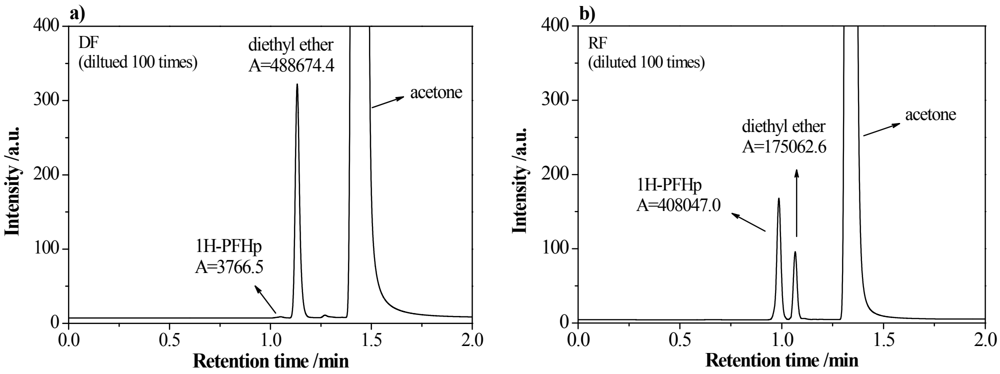

Figure S5. GC profiles of recovered distilled fraction (DF) and residual fraction (RF) during the isolation of 1H-PFHp. Prior to GC analysis, both DF and RF were diluted with acetone by 100 times. According to eqs. S2 and S4, the f_m of 1H-PFHp to diethyl ether was calculated to be 3.6, which was employed to accesses the relative distribution of components in both distillates and residual fraction. It was observed that only 2.7% of 1H-PFHp was distilled off in the DF, and the isolated 1H-1-PFHp in RF possessed a purity >85%.

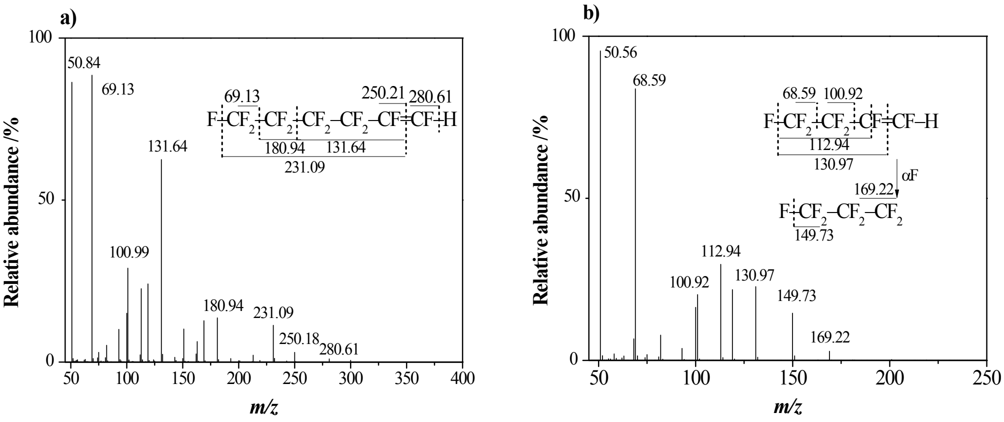

Figure S6. GC/MS profiles of majority products after 2 h of ball milling of $C_6F_{13}COOH$ (a) and C_4F_9COOH (b) with alumina. Acetone was used as the extraction agent.

DR-FTIR spectra of Al−F bonds

Al_2O_3 and the mixture of PFOA and Al_2O_3 before and after the 5-min milling treatment at rotation speeds of 50 and 100 rpm were characterized by DR-FTIR spectroscopy, respectively. Figure S7 also showed DR-FTIR spectra of the Al_2O_3-NaF mixture before and after 5-min milling as references. As the rotation speed was increased to 100 rpm, the milled Al_2O_3-PFOA mixture at 100 rpm exhibited a new peak at 1021 cm^{-1}. The same peak also appeared at the same wavenumber in the spectrum of the Al_2O_3-NaF mixture after the 5-min milling treatment at a rotation speed of 50 rpm, but not found in the case of Al_2O_3 alone under the same milling conditions. Thus, the new peak at 1021 cm^{-1} in the DR-FTIR profile of milled Al_2O_3-PFOA mixture could be assigned to the formation of Al−F between Lewis acid sites and the released fluoride ions.

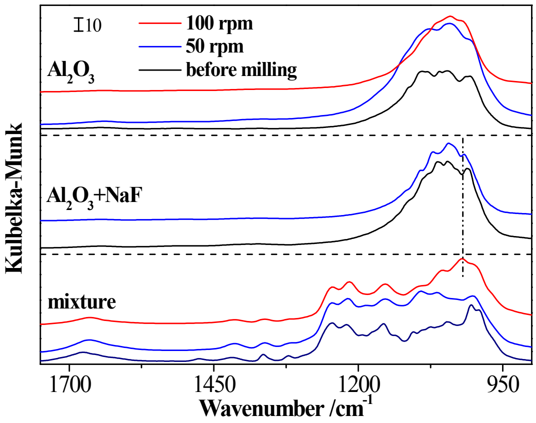

Figure S7. DR-FTIR spectra of Al_2O_3 and the mixtures of PFOA-Al_2O_3 and Al_2O_3-NaF before (black line) and after the 5-min milling treatment at rotation speeds of 50 (blue line) and 100 (red line) rpm.

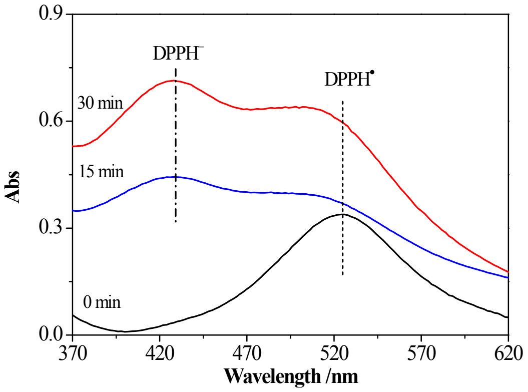

Figure S8. UV-Vis absorption changes of extraction solution with dimethyl sulfoxide (DMSO) for the test on co-milled DPPH$^•$ with Al_2O_3 at different milling time. Before ball milling, the extracted DPPH$^•$ solution showed a characteristic absorption peak at 525 nm. After ball milling, it was observed a new peak centered at 425 nm, which could be attributed to anionic form DPPH$^-$. Thus, the ball milling process can generate free electrons on mechanically activated alumina surfaces. This can be explained by that lattice oxide of metal oxides can volatilize as molecular oxygen, and oxygen vacancies were simultaneously formed in the lattice as well as releasing two electrons during high energy milling.

DR-FTIR spectra of thermal treatment of Alumina

DR-FTIR spectra of the heated alumina after 30-min heat treatments at 25 and 150 °C in the absence of PFOA are also provided as references. As shown in Figure S9, only the loss of the characteristic absorption of the surface OH groups (3200~3700 cm^{-1}) on the alumina was observed in the profile of the heated alumina in the absence of PFOA.

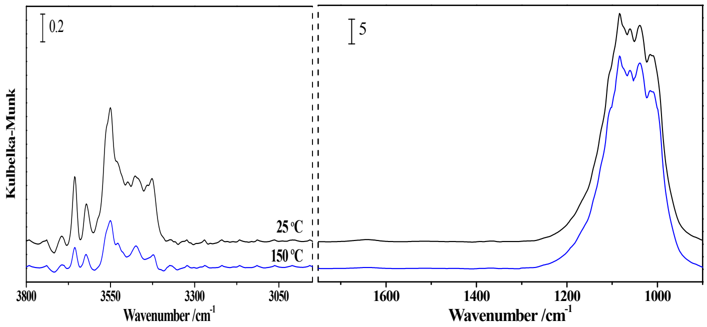

Figure S9. DR-FTIR spectra of Al_2O_3 after 30-min thermal treatments at 25 and 150 °C.

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