Supporting Information

Tribochemical Degradation of Polytetrafluoroethylene in Water and Generation of Nanoplastics

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Totals – 23 pages, 21 figures, 1 table

Name	Table of contents	Page No.
	Materials and Methods	S2-S3
Table S1	A brief summary of the degradation of PTFE with metal concentration in solution	S4
Figure S1	Photograph of PTFE degradation by different metals	S5
Figure S2	Photograph of PTFE magnetic pellet	S5
Figure S3	SEM/EDS of the PTFE-gold polymeric film	S6
Figure S4	SEM/EDS of the copper derived PTFE polymeric film	S7
Figure S5	SEM/EDS of the copper derived PTFE polymeric film in the cracks	S8
Figure S6	SEM/EDS of the brass derived PTFE polymeric film	S9
Figure S7	SEM/EDS of the silver-derived PTFE polymeric film	S10
Figure S8	Expanded view of the peaks for stainless steel and copper PTFE materials	S10
Figure S9	Independent Raman measurements	S11
Figure S10	Expanded view of the peaks for stainless steel and copper PTFE materials	S12
Figure S11	Reactions of PTFE with metal ions	S13
Figure S12	HRESI MS of the solution from brass vessel	S14

Figure S13	HRESI MS of the solution derived from a copper vessel in presence of $CuCl_2$ without glucose	S15
Figure S14	SEM/EDS of the copper derived PTFE polymeric film, after reaction with γ-cyclodextrin solution	S16
Figure S15	Plot of amounts of solid material separated from a copper vessel vs time, after reaction with γ-cyclodextrin solution	S17
Figure S16	TEM images of the nanoplastics after reaction	S18
Figure S17	SEM/EDS of the plastics particles after reaction	S19
Figure S18	Reaction of polypropylene with glucose solution in copper vessel	S20
Figure S19	Raman spectra of polypropylene from a copper vessel	S21
Figure S20	Expanded view of the Raman spectra	S22
Figure S21	SEM/EDS of the copper-derived polypropylene polymeric film	S23

Materials and Methods

Methods

Chemicals and Materials: Vessels of copper, silver (with 90.50% purity), brass (60.66% copper, 36.58% zinc), stainless steel and polypropylene were purchased from the local market. (D+)-glucose (G), γ-CD (cyclodextrin), magnetic pellet and gold foil were purchased from Sigma-Aldrich. Milli-Q water was used throughout the experiment. Experiments were performed with various types of PTFE samples (from local and Sigma Aldrich) to ensure that source of the samples did not affect the results. Experiments were repeated with magnetic pellets (coated with PTFE) as well as different forms of PTFE (tape, granules and sheet).

Experimental methods:

For the reaction between gold surface and PTFE, a 2 cm × 2 cm gold foil was inserted into a 250 mL PTFE beaker containing 100 mL aqueous solution of glucose (~1 mg/mL) having a PTFE coated magnetic pellet at 60-70˚C. Samples were collected at regular intervals for inductively coupled plasma mass spectrometry (ICP MS) and other analyses.

We measured the weight of the PTFE pellet after taking out the magnet from it.

γ-CD/glucose (~70 mg) was placed in silver, copper, brass and stainless steel vessels in milli-Q water (70 mL). The reaction mixtures were kept stirring at 60-70 °C for 15 days. Samples were collected at regular intervals for ICP MS and other analyses.

For the reaction of polypropylene, a magnetic pellet was inserted into the polypropylene vial (Figure S16). Reaction conditions were same as of PTFE.

Instrumentation:

ICP MS: ICP MS was performed using Perkin Elmer NexION 300X instrument equipped with Ar plasma. Before analysing any sample, the instrument was first calibrated with Au standard of four different concentrations (0, 10, 100, and 1000 ppb) to get a calibration curve with R2=0.9999. Calibration was done with other elemental standards also.

ESI MS:

The fluorocarbon species were studied by Waters Synapt G2Si HDMS instrument. Optimized conditions for these measurements were as follows: Flow rate: 30-50 μL/min, capillary voltage: 3 kV, cone voltage: 80-120 V, source offset: 100-130 V, desolvation gas flow: 400 L/h.

Spectroscopy:

Raman spectroscopic measurements were performed in a Witec GmbH, Alpha-SNOM alpha300 S confocal Raman instrument equipped with a 532 nm laser as the excitation source.

Microscopy:

SEM (scanning electron microscopy) and energy dispersive analysis of X-rays (EDS) were performed using an FEI QUANTA-200 SEM.

HRTEM (high resolution transmission electron microscopy) was performed with a JEOL 3010, 300 kV instrument equipped with a UHR polepiece.

XPS:

XPS measurements were carried out with an Omicron ESCA Probe Spectrometer. It consists of EA 125 energy analyzer, XM 1000 MkII X-ray source and monochromator, DAR 400 X-ray source (Al/Mg), VUV source HIS 13, CN 10 and CN 10+ charge neutralizer system, ISE 10 sputter ion source and MKS residual gas analyzer for TPD. Polychromatic Al Kα X-rays ($h\gamma$ = 1486.6 eV) were used for analysis. 300 W X-ray power was applied.

Charge measurement:

We took a PTFE beaker containing 100 mL milli-Q water. A magnetic pellet covered with copper foil was immersed in the beaker (Figure 4). Magnetic pellet was rotated at 60-70 °C. We took 1 mL water from the beaker at ~ 30 seconds interval and measured the charge of this water using a home-built Faraday cup and an electrometer.

Table S1. Concentration of metals from the solution of their corresponding vessels, analyzed by ICP MS. Amount of solid material separated from each vessel is also given.

Metal vessel	Metal	Time	Metal ion concentration (ppm)	Amount of metal-PTFE (mg)
Copper	Cu	Day 03	153.2	12.00
		Day 06	223.0	23.00
		Day 09	291.1	33.00
		Day 12	347.8	42.00
		Day 15	419.3	53.00
Brass	Zn	Day 03	78.5	05.00
		Day 06	109.5	09.00
		Day 09	132.8	14.00
		Day 12	167.3	19.00
		Day 15	195.8	23.00
Silver	Ag	Day 03	0.4	01.00
		Day 06	0.7	01.75
		Day 09	0.9	02.50
		Day 12	1.3	03.50
		Day 15	1.9	05.00
Stainless steel	Fe	Day 03	0.3	00.75
		Day 06	0.5	01.40
		Day 09	0.7	02.00
		Day 12	1.1	02.70
		Day 15	1.3	03.50

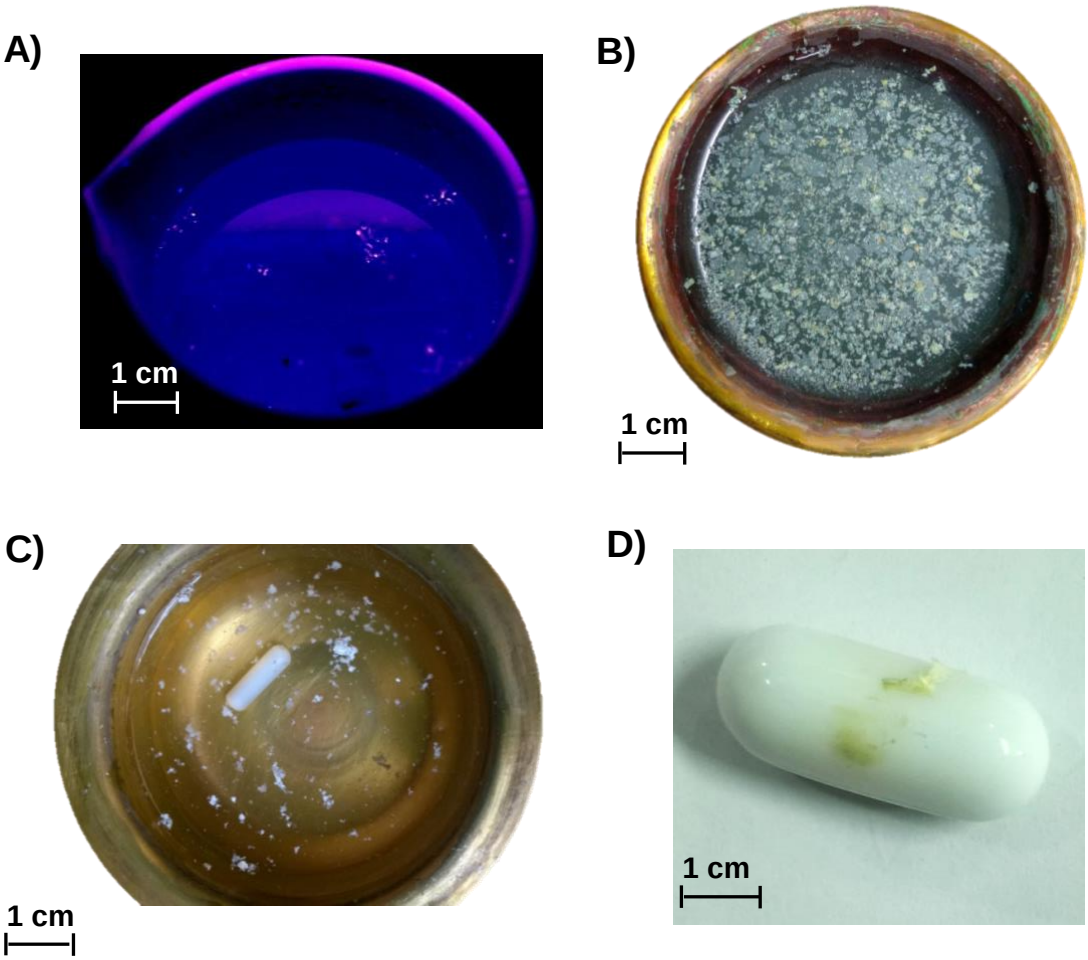


Figure S1. Photograph of PTFE degradation by different metals. A), B) and C) correspond to gold foil, copper and brass vessel, respectively. A) Red luminescent polymeric films appearing on the liquid surface after reaction with gold foil. D) Color of the PTFE-metal polymeric films after reaction in copper vessels.

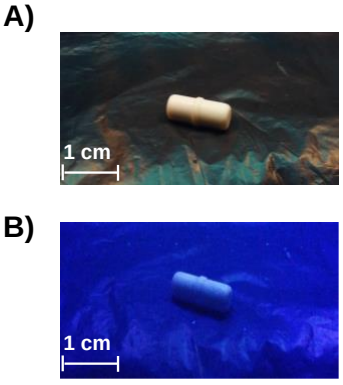
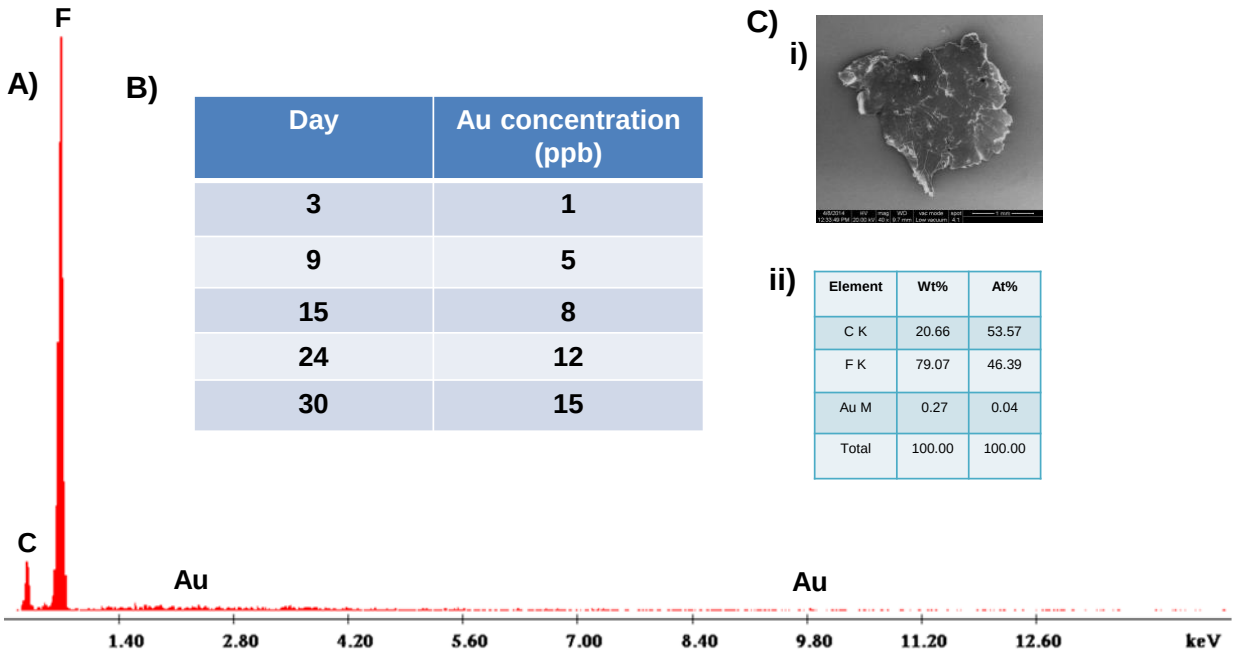


Figure S2. Photographs of the PTFE covered magnetic pellet A) under visible light and B) UV light (mercury vapor lamp).

A)



B)

Day	Au concentration (ppb)
3	1
9	5
15	8
24	12
30	15

C)

i)

ii)

Element	Wt%	At%
C K	20.66	53.57
F K	79.07	46.39
Au M	0.27	0.04
Total	100.00	100.00

Figure S3. SEM/EDS of the PTFE-gold polymeric film. A) EDS of the PTFE-gold polymeric film. B) Extraction of gold by glucose in the course of 30 days. SEM image and elemental analysis data are presented in C) i) and ii), respectively. As we have performed the SEM/EDS on a carbon tape, the % of carbon will be different from the expected value.

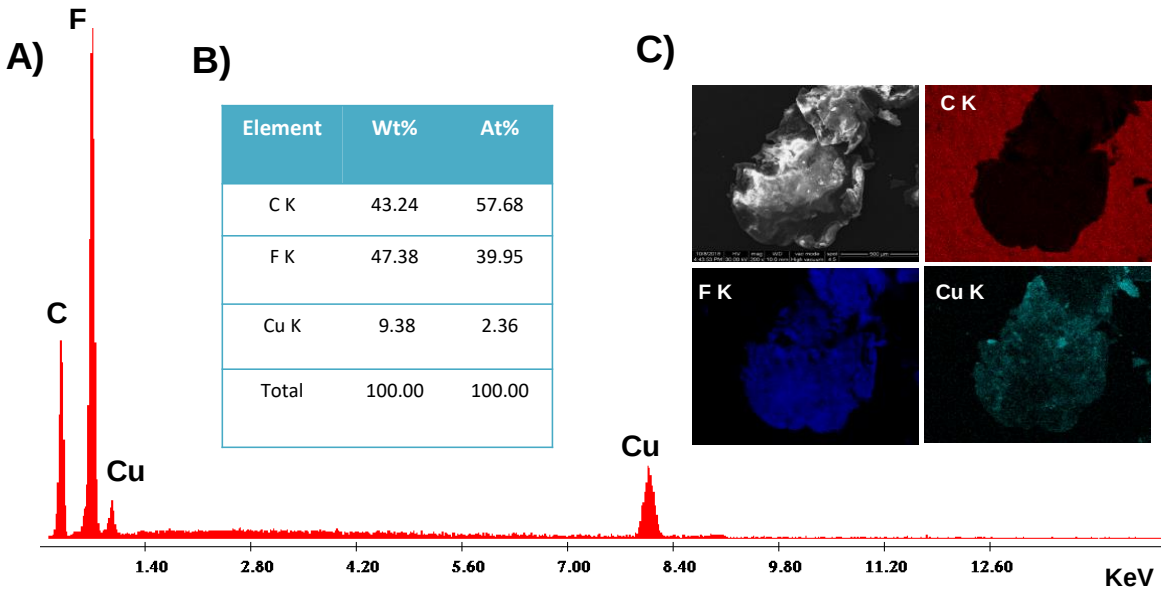
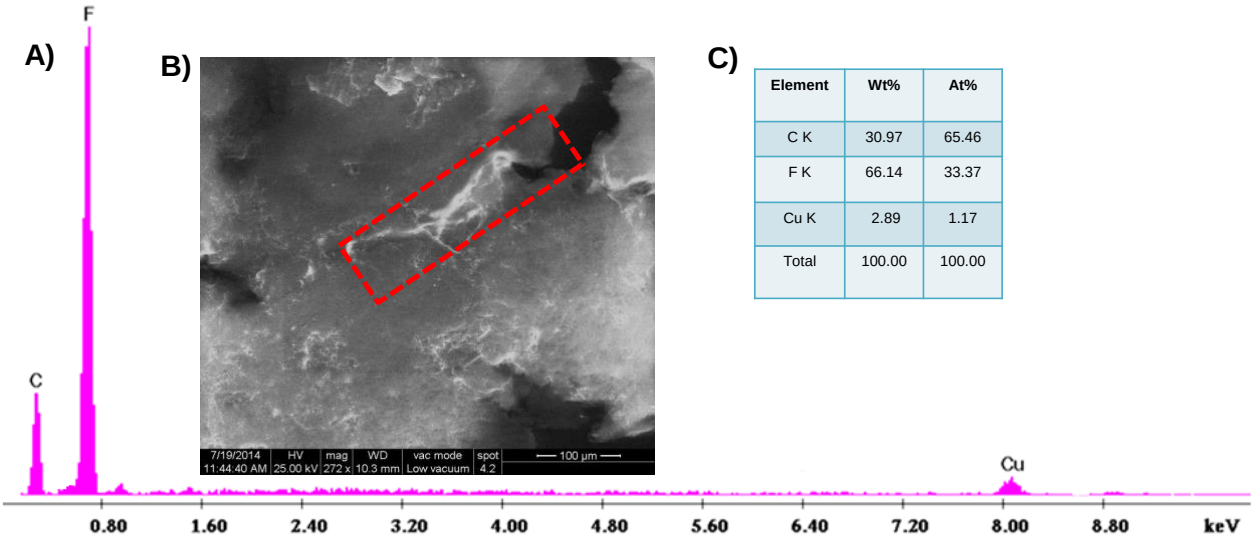


Figure S4. SEM/EDS of the copper derived PTFE polymeric film. A) EDS of the copper derived PTFE polymeric film. B) Elemental analysis, showing the presence of copper and fluorine. C) Elemental mapping of the material. Scale bar is the same for all images in C).

A)

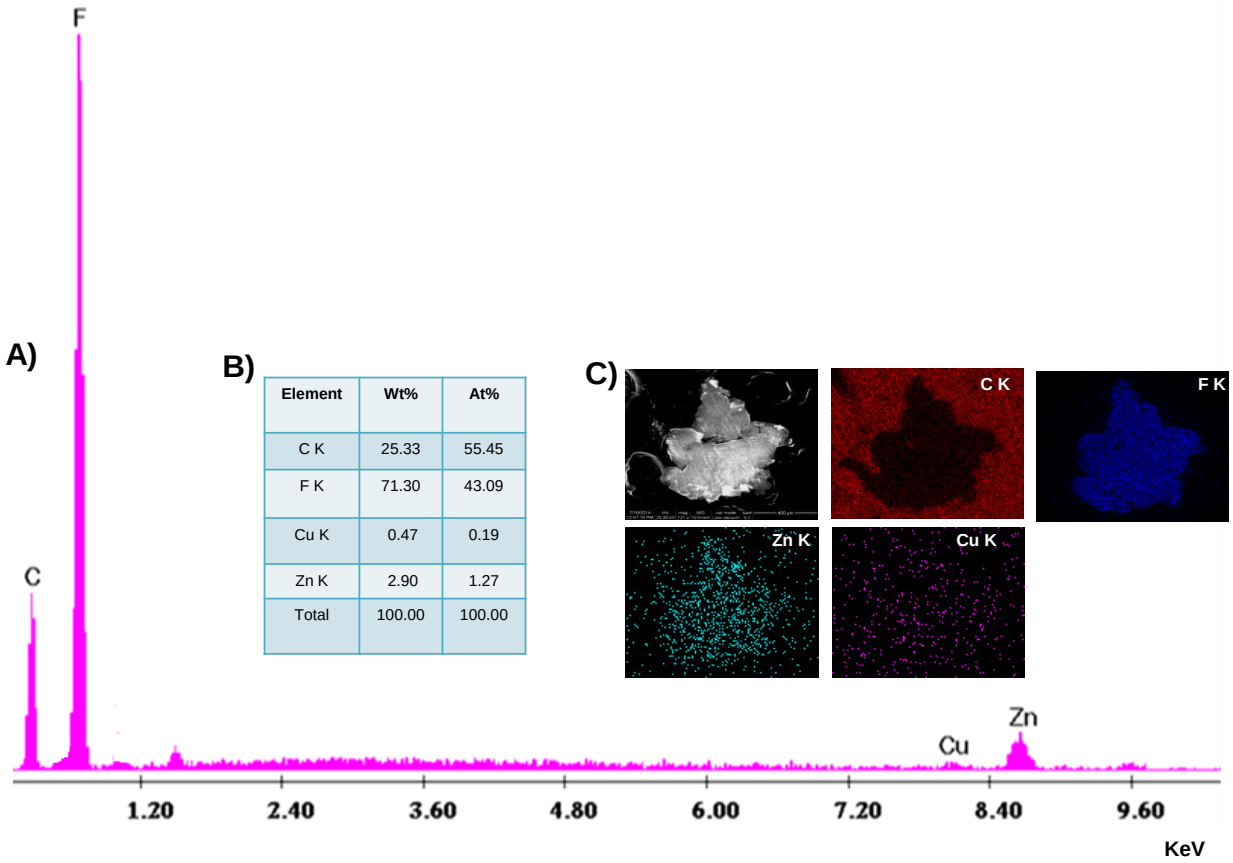


B)

C)

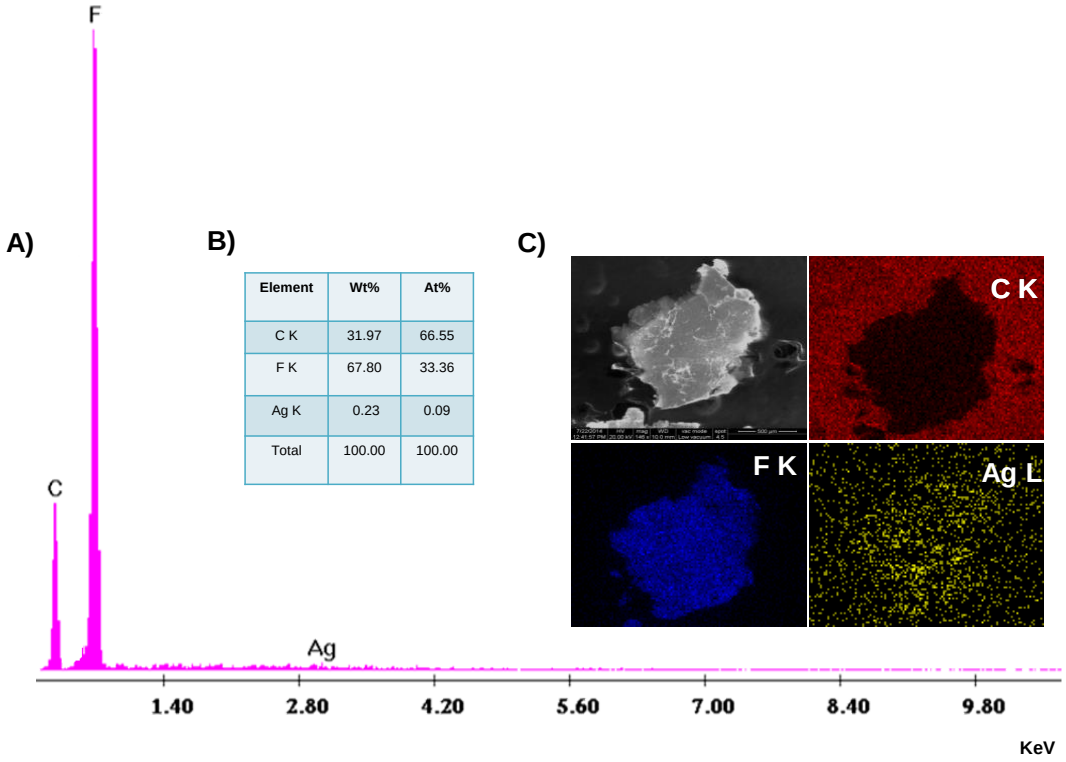
Element	Wt%	At%
C K	30.97	65.46
F K	66.14	33.37
Cu K	2.89	1.17
Total	100.00	100.00

Figure S5. SEM/EDS of the copper derived PTFE polymeric film. A) SEM EDS, B) SEM image and C) elemental analysis of the polymeric film at the cracks. Presence of copper was detected from these cracks.



Element	Wt%	At%
C K	25.33	55.45
F K	71.30	43.09
Cu K	0.47	0.19
Zn K	2.90	1.27
Total	100.00	100.00

Figure S6. SEM/EDS of the brass derived PTFE polymeric film. A) EDS of the brass derived PTFE polymeric film. B) Elemental analysis, showing the presence of copper, zinc and fluorine. C) Elemental mapping of the material. Scale bar is the same for all images in C).



Element	Wt%	At%
C K	31.97	66.55
F K	67.80	33.36
Ag K	0.23	0.09
Total	100.00	100.00

Figure S7. SEM/EDS of the silver derived PTFE polymeric film. A) SEM EDS of the silver derived PTFE polymeric film. B) Elemental analysis, showing the presence of silver and fluorine. C) Elemental mapping of the material. Scale bar is the same for all images in C).

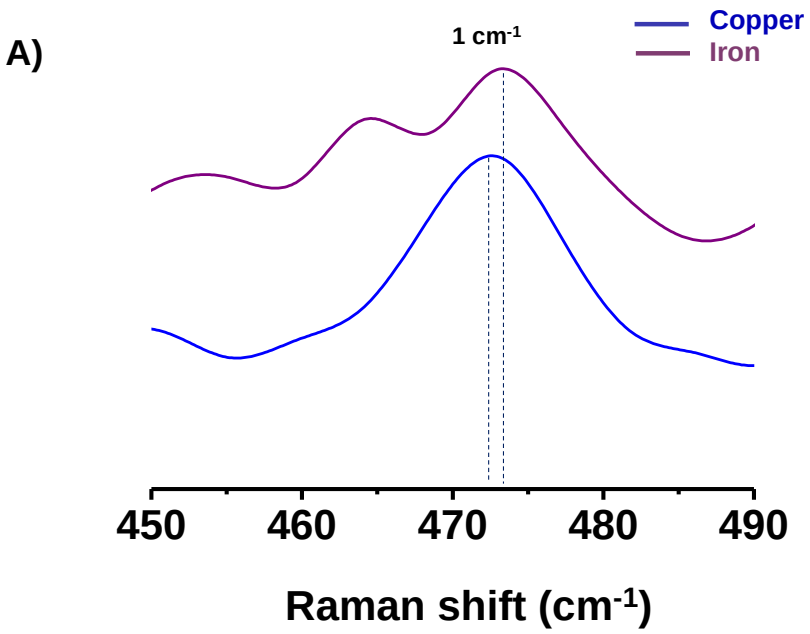


Figure S8. Raman Spectra of the PTFE-metal composite. A) Expanded view of the peaks at 473 and 472 cm^{-1} for stainless steel (purple) and copper (blue) PTFE material, respectively from Figure 2. A shift of 1 cm^{-1} was observed for copper and iron-containing samples, respectively.

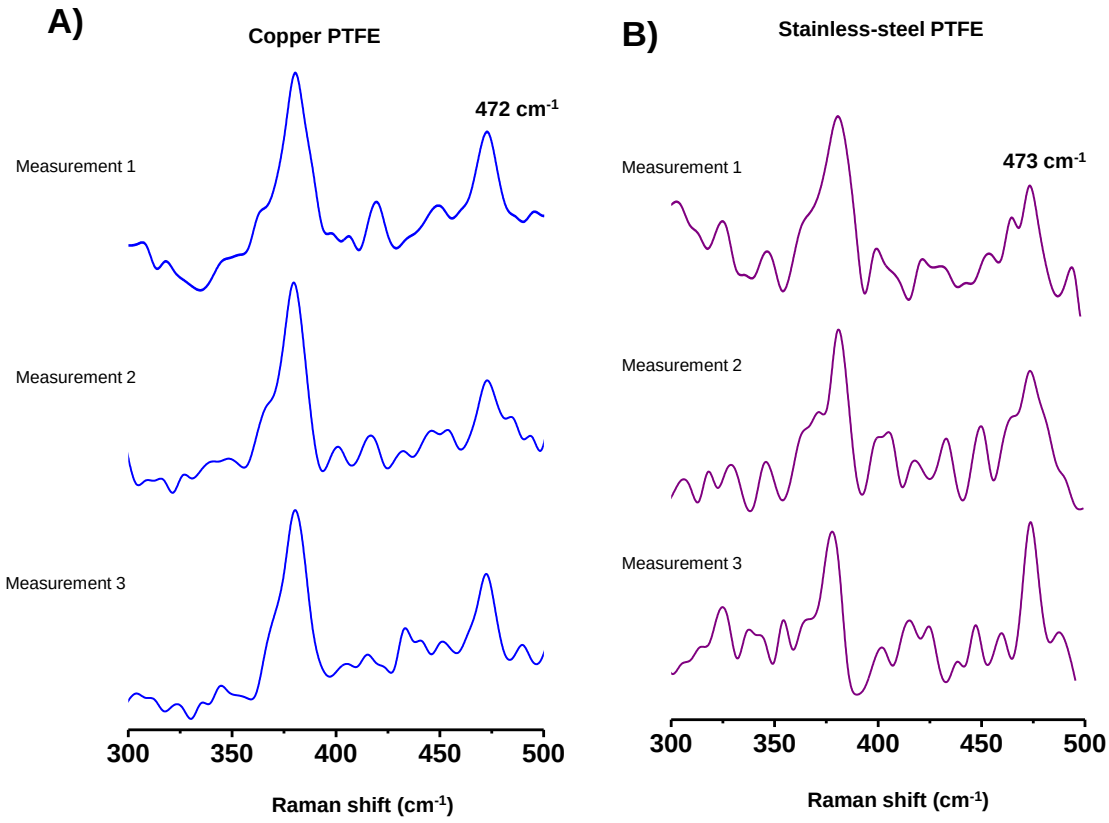


Figure S9. Independent Raman measurements from the polymer separated from A) copper PTFE and B) stainless-steel PTFE experiments. Peaks due to the polymer are reproduced in all measurements.

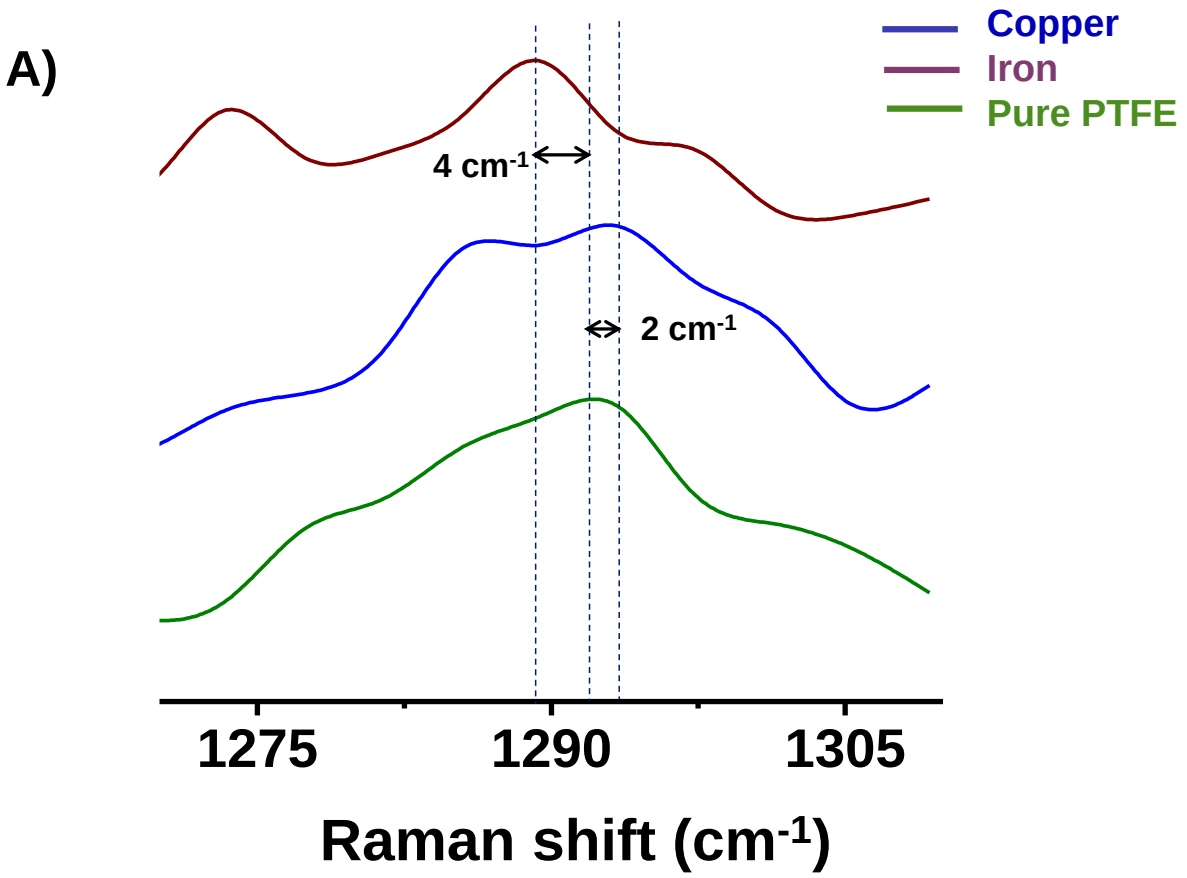


Figure S10. Raman Spectra of the PTFE-metal composite. A) Expanded view of peak 6 of Figure 2. Shifts of 2 and 4 cm^{-1} were observed for the C-C stretching (peak 6) for copper and iron-containing samples, respectively compared to pure PTFE.

A) B)

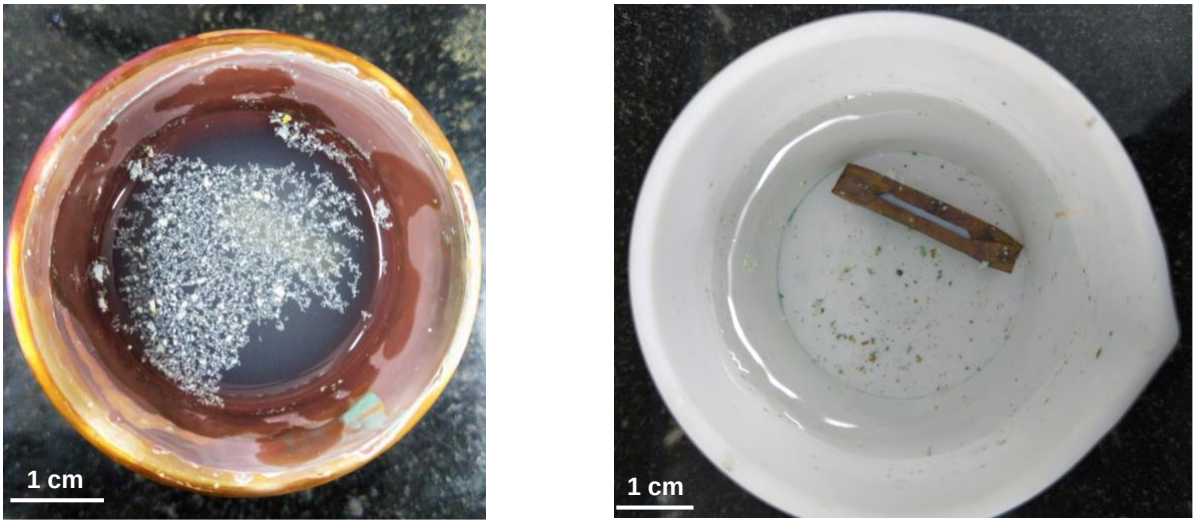


Figure S11. Reaction of PTFE pellet with copper chloride. Reaction of copper chloride solution (20 mg $CuCl_2$ in 50 mL water) with PTFE magnetic pellet in copper vessel A) and PTFE beaker B). Similar kind of degradation has been observed for copper (II) ions. Greenish blue color PTFE-metal composite has been observed. This reaction was performed without glucose.

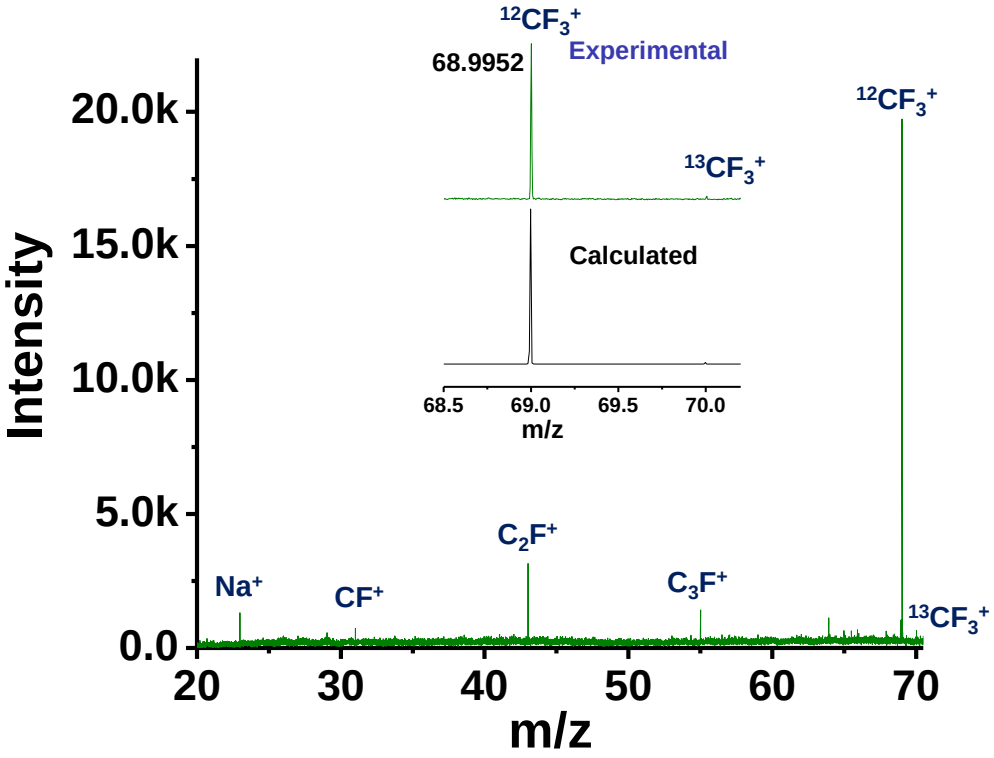


Figure S12. HRESI MS of the solution from brass vessel. Presence of the fluorocarbon species has been confirmed. Inset of Figure S12 shows the calculated and experimental mass spectra of CF_3^+.

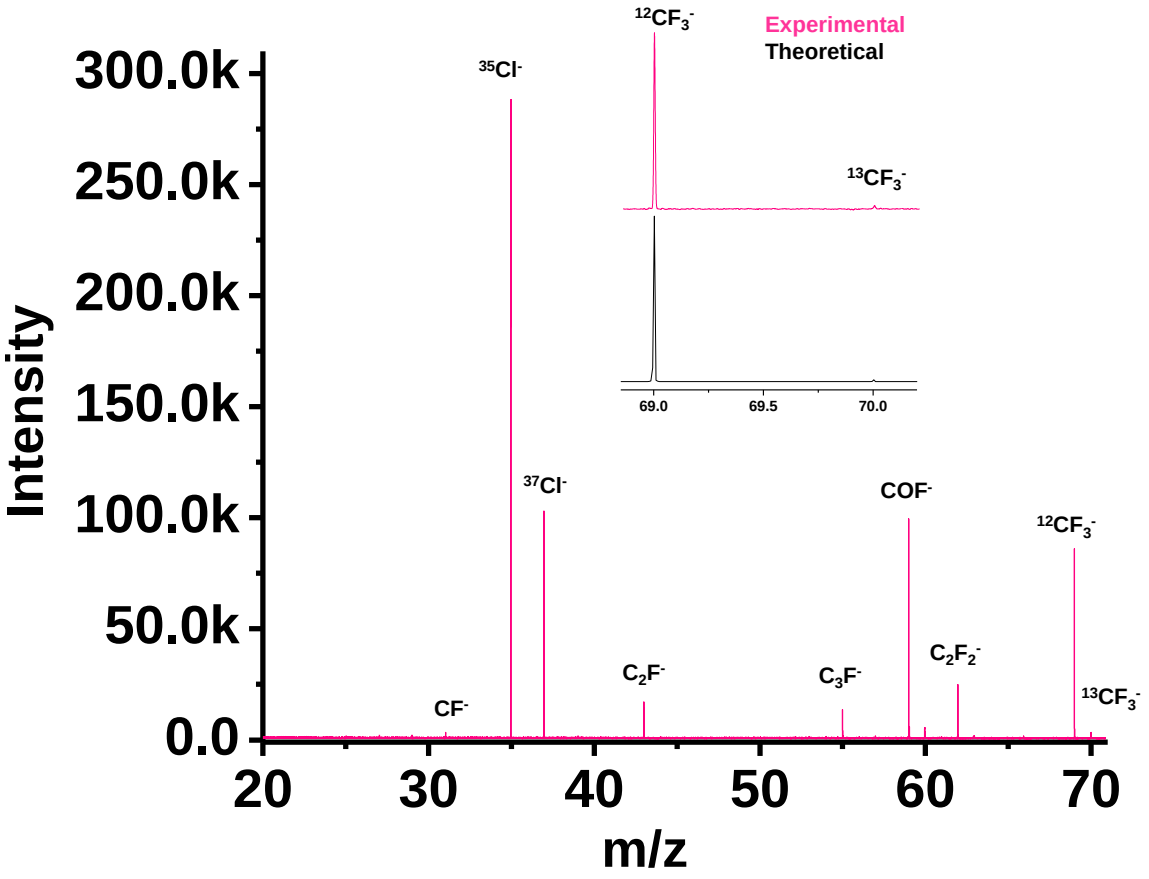
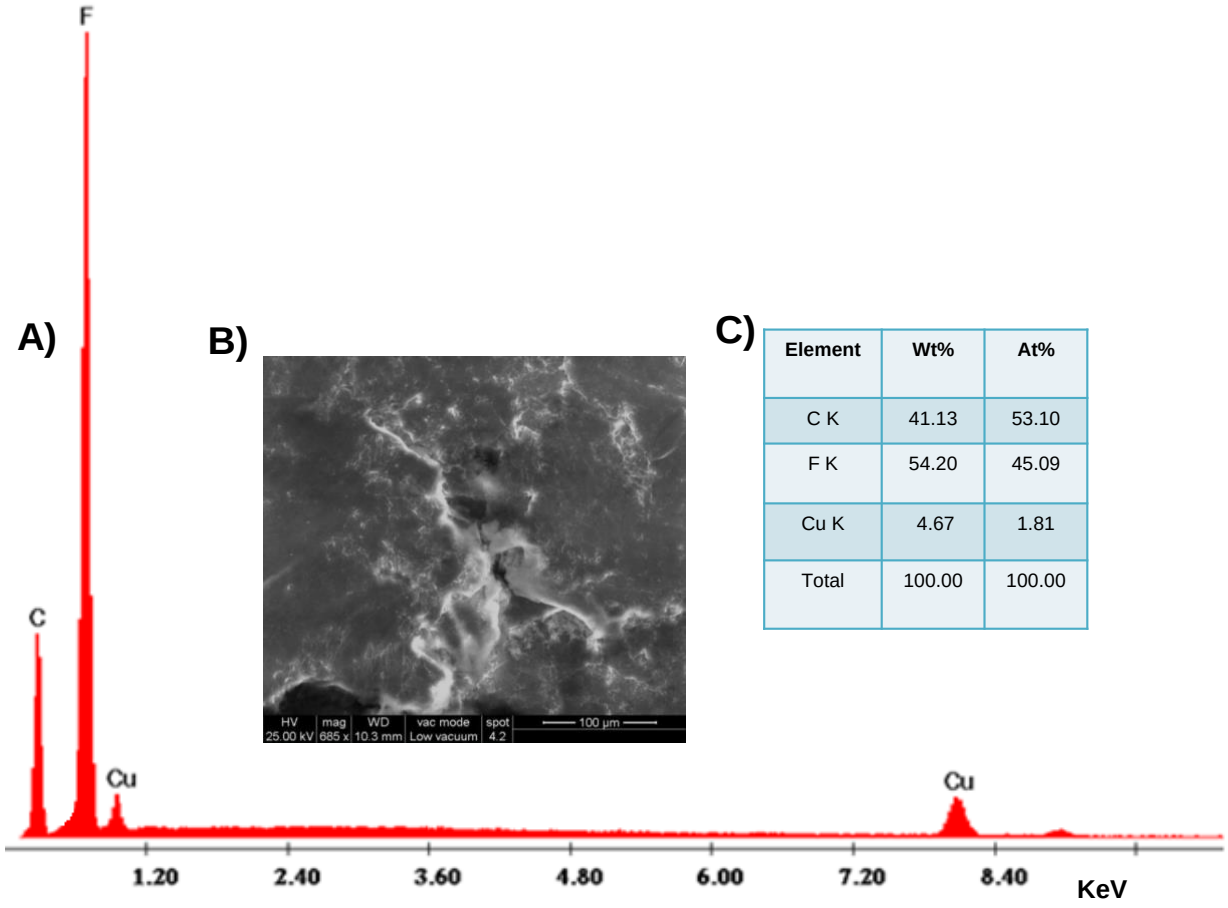


Figure S13. HRESI MS of the solution derived from a copper vessel in presence of $CuCl_2$ without glucose. Presence of various fluorocarbon species in solution was identified by mass spectrometry. Inset of Figure S13 shows the calculated and experimental mass spectra of CF_3^-.



Element	Wt%	At%
C K	41.13	53.10
F K	54.20	45.09
Cu K	4.67	1.81
Total	100.00	100.00

Figure S14. SEM/EDS of the copper derived PTFE polymeric film. A) SEM/EDS B) SEM image and C) elemental EDS of the material from copper derived PTFE, after reaction using γ-cyclodextrin. Presence of copper and fluorine was noticed.

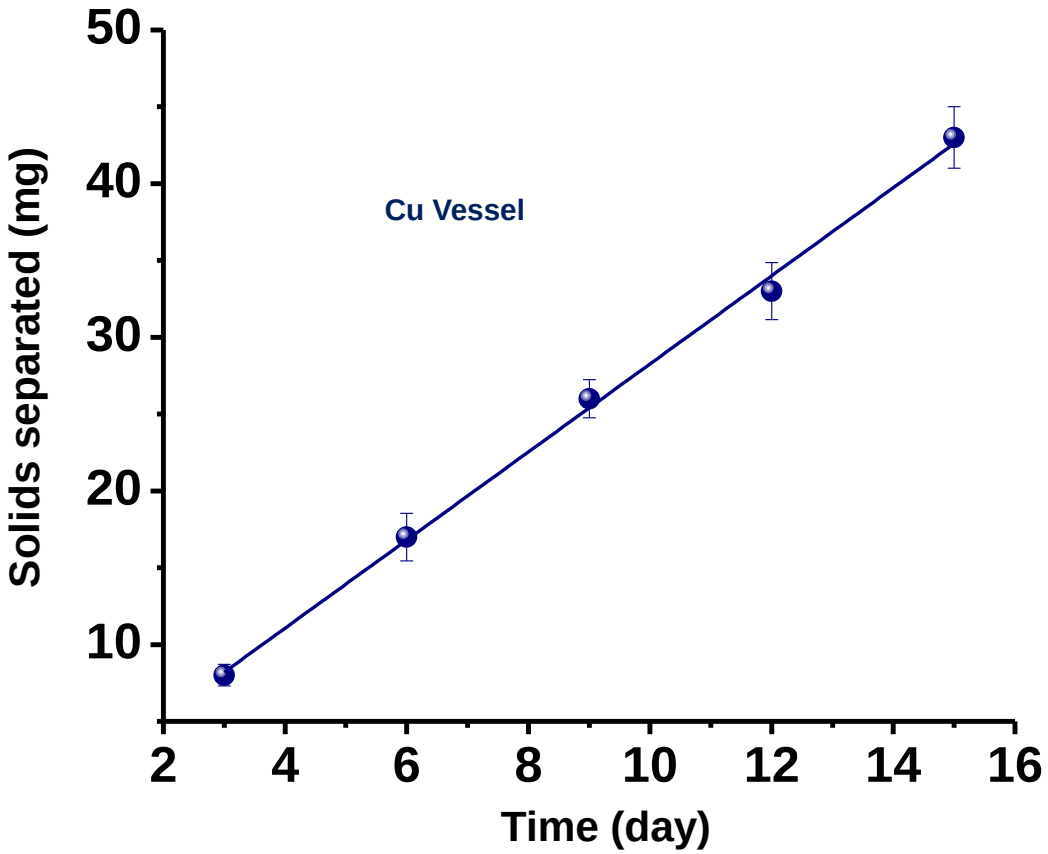


Figure S15. Amount of solid material separated from a copper vessel plotted as a function of time, after reaction with γ-cyclodextrin.

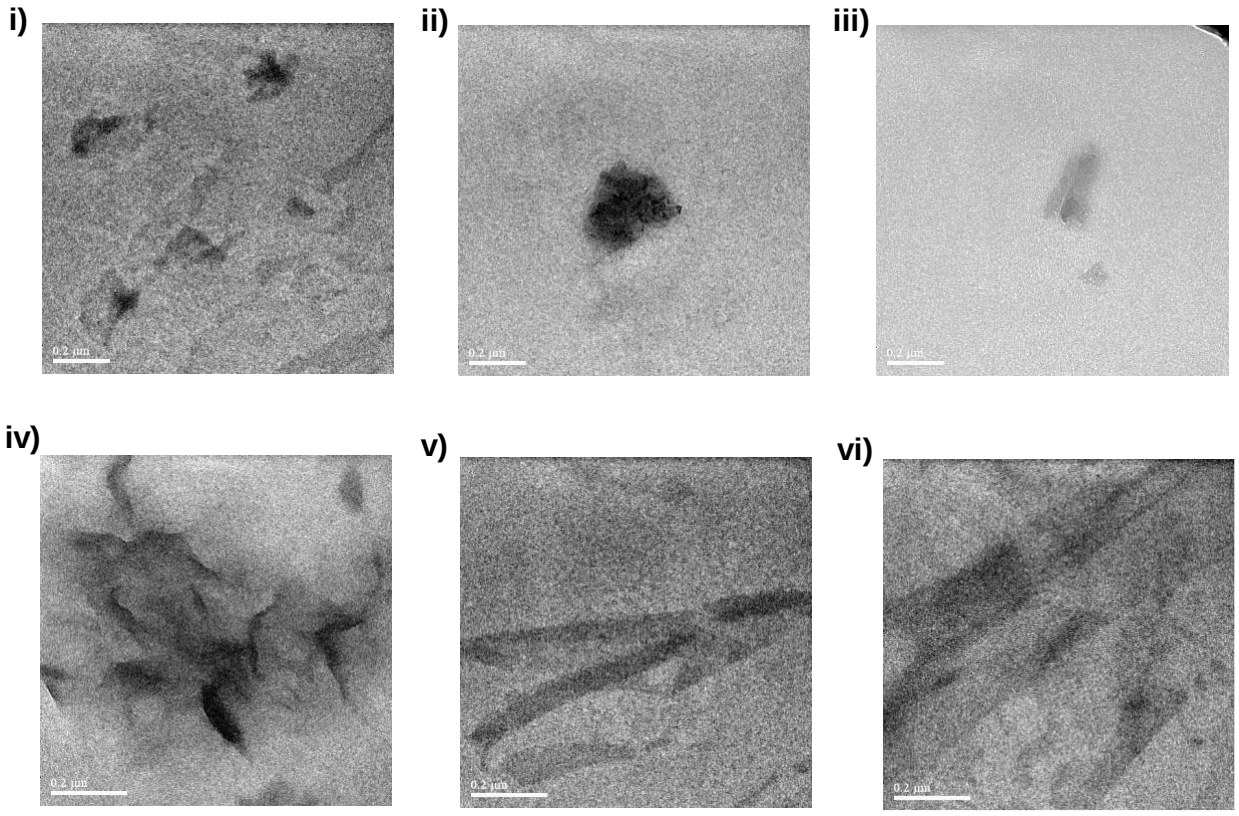
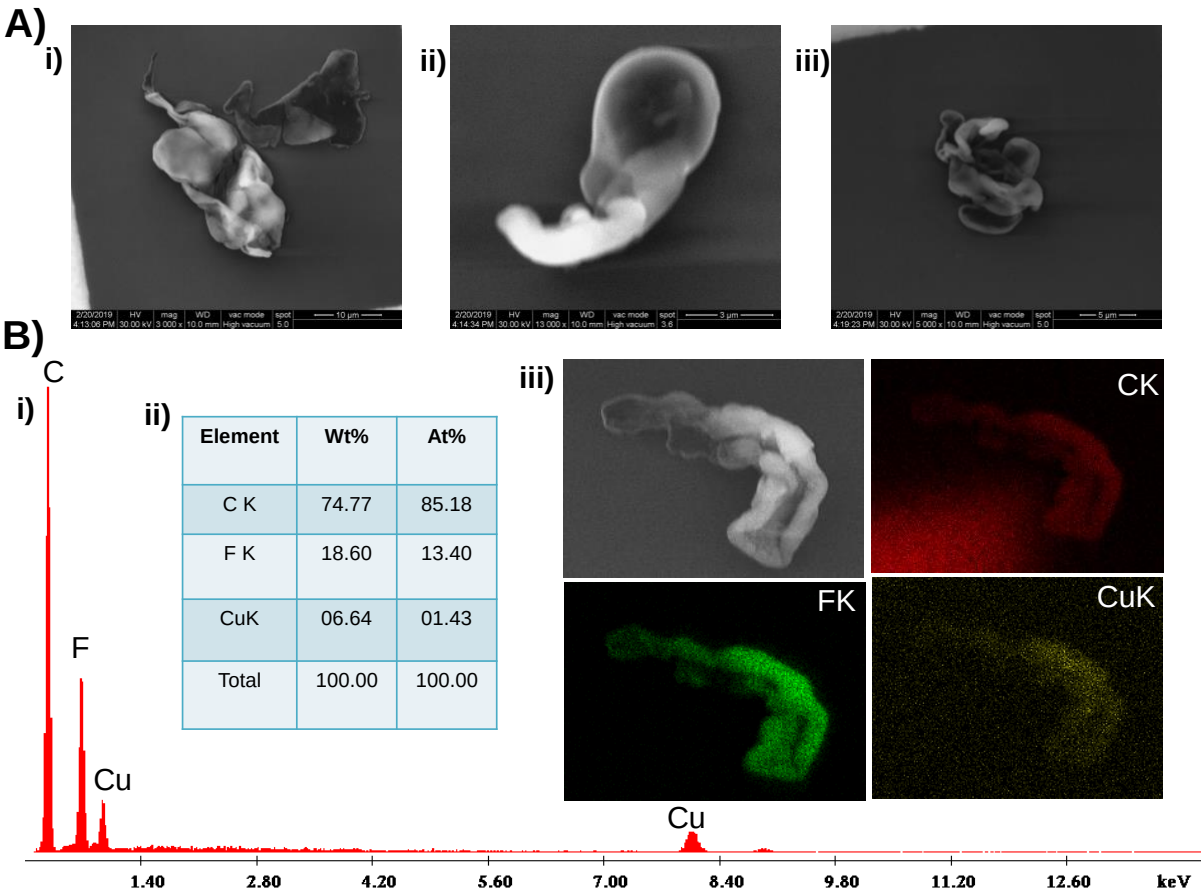


Figure S16. i-vi TEM images of the nanoplastics with different sizes, varying from 200-400 nm. Images from different regions of the grid are presented.



Element	Wt%	At%
C K	74.77	85.18
F K	18.60	13.40
CuK	06.64	01.43
Total	100.00	100.00

Figure S17. A) i-iii) SEM images of the plastic particles of different sizes varying from 4-10 µm. B) i)-ii) Elemental analyses, showing the presence of copper and fluorine. iii) Elemental mapping of the plastic particles. Scale bars in iii) are the same as in the SEM images. The percentage of carbon will be different from the expected value because we have performed the analysis on a carbon coated copper grid. By the interaction of copper ions with charged PTFE surface, the fluorocarbon species could come into the solution.

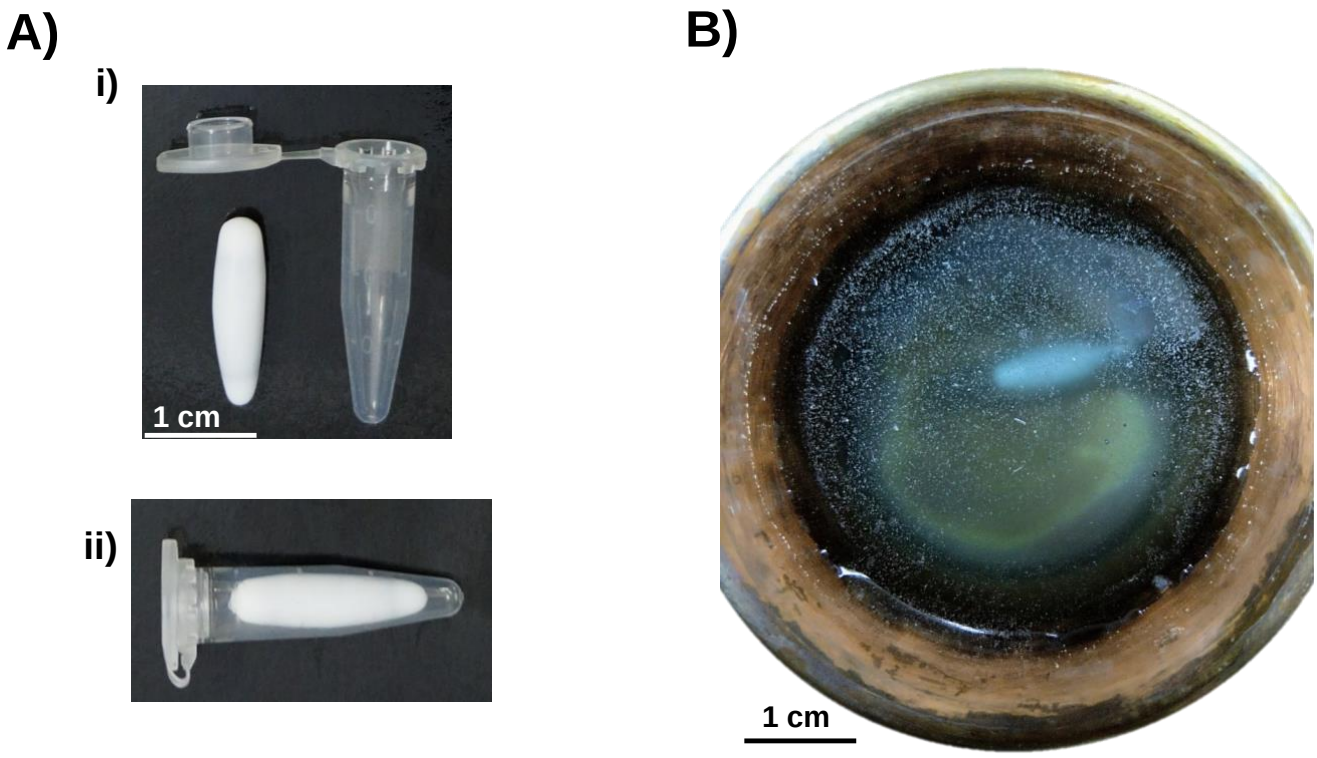


Figure S18. A) i) Photograph of the polypropylene vial. ii) A magnetic pellet was inserted into this vial. B) Reaction of polypropylene with glucose solution in copper vessel which was stirred to cause degradation. Degradation of polypropylene was noticed after 10 days of reaction. Spectroscopic and elemental analysis of the floating materials are presented in Figure S19–S20 and Figure S21, respectively.

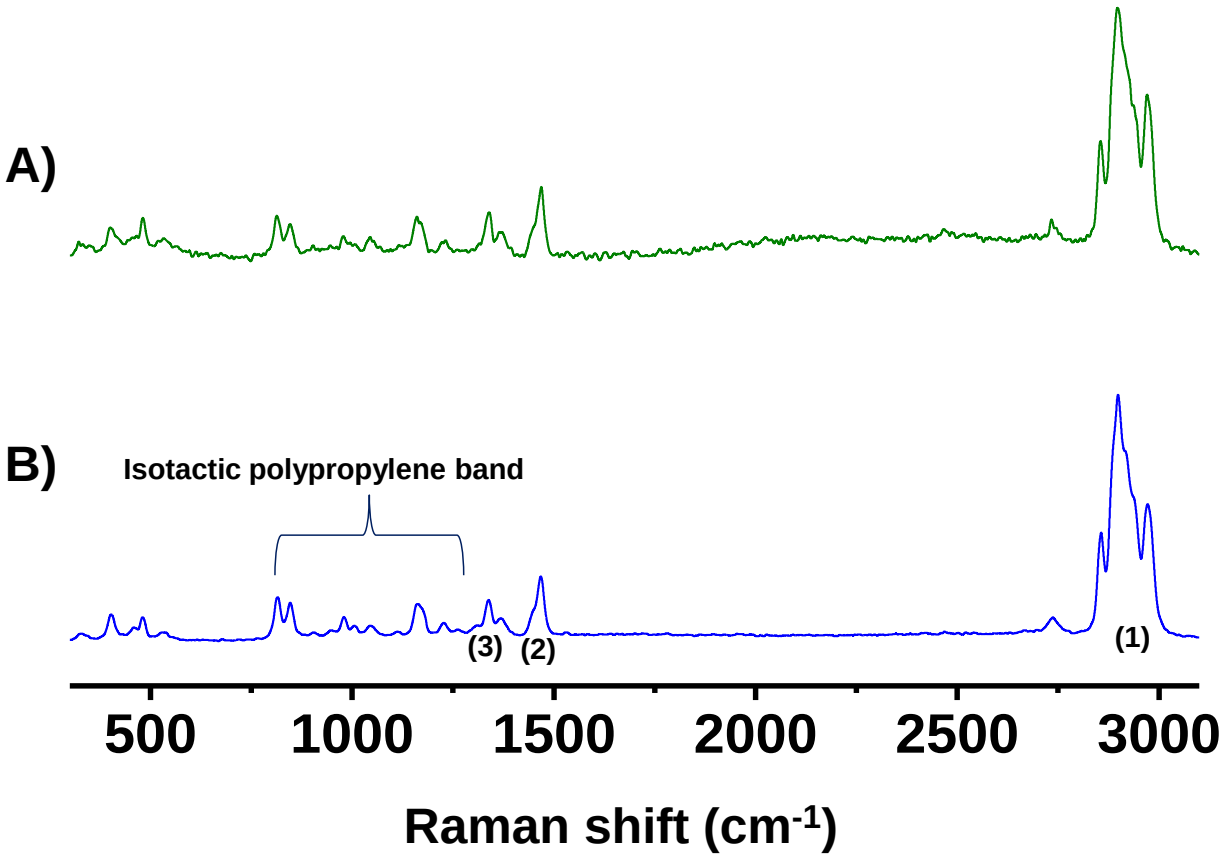


Figure S19. Raman spectra of the polypropylene-copper composite (A) and that of pure polyrpropylene (B). Peaks 1, 2, and 3 represent C-H stretching, CH_2 deformation, and symmetric CH_3 deformation.

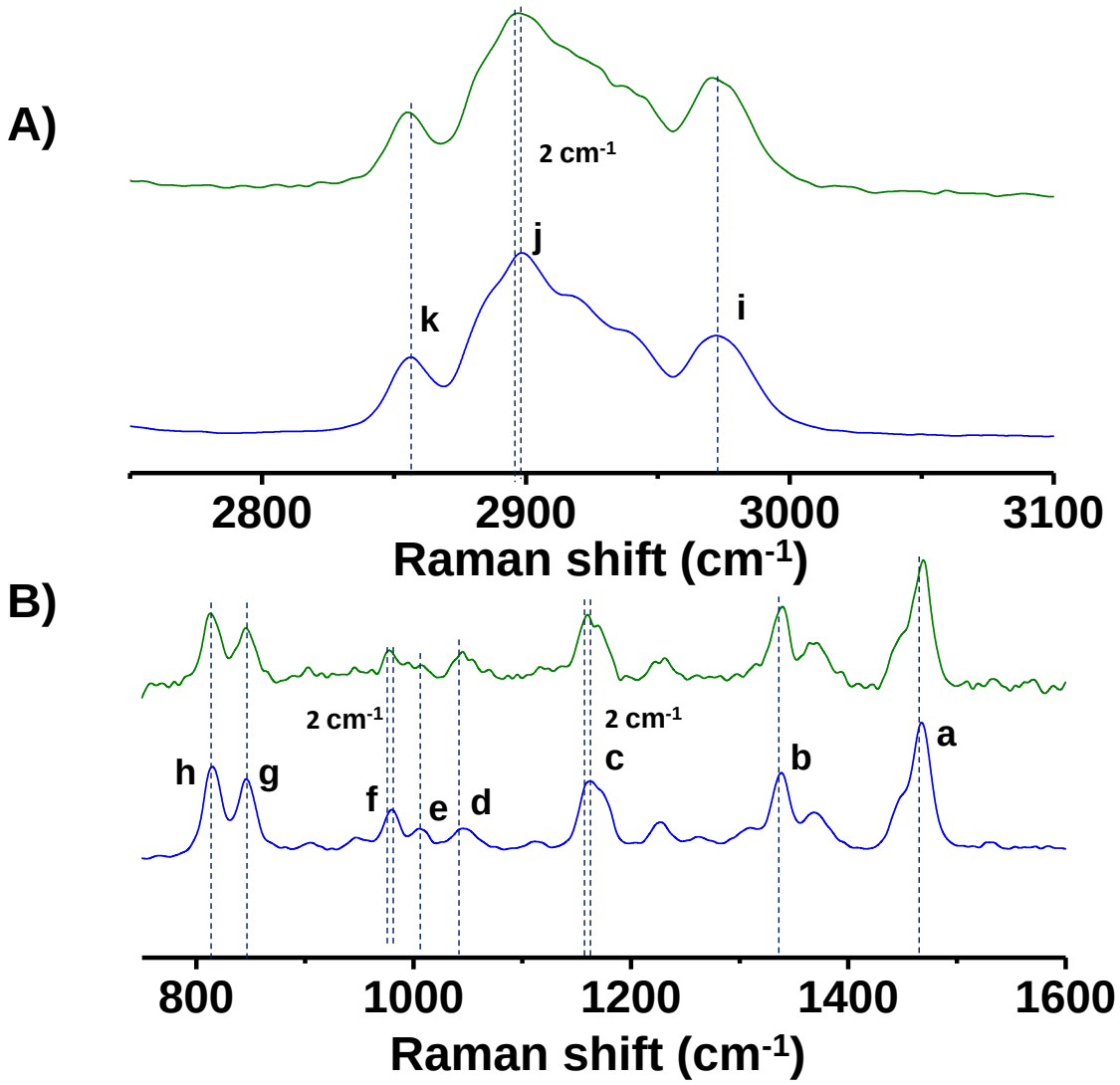
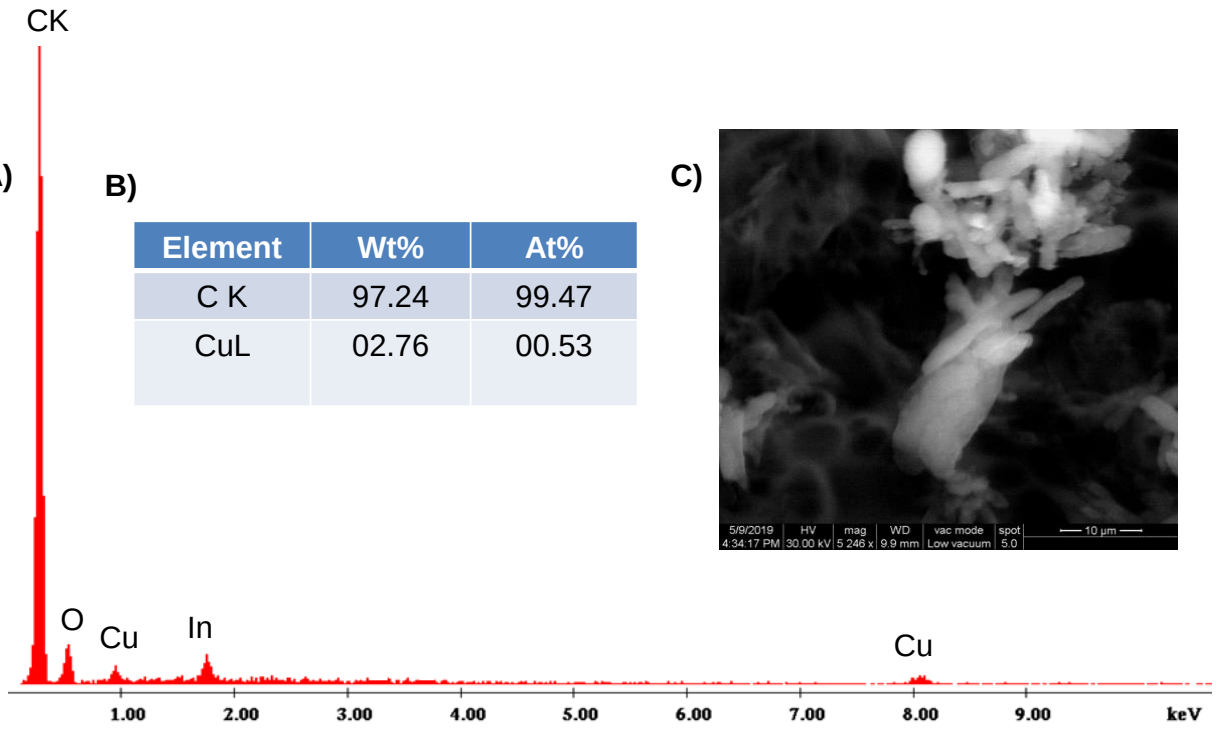


Figure S20. Expanded views of the Raman spectra of the same samples as in Figure 19. Spectral colors correspond to the same as in Figure 19. Peaks c, f, and j show 2 cm^{-1} shift. Peak splitting was observed in the case of c.

A)



B)

Element	Wt%	At%
C K	97.24	99.47
CuL	02.76	00.53

C)

Figure S21. A) SEM/EDS of the copper-derived polypropylene polymeric film. B) Elemental analysis, showing the presence of copper and carbon. Other peaks are because of the ITO plate used as the substrate. C) Image of plastic particles of polypropylene found in the solution.