



BIOLOGY ZERO

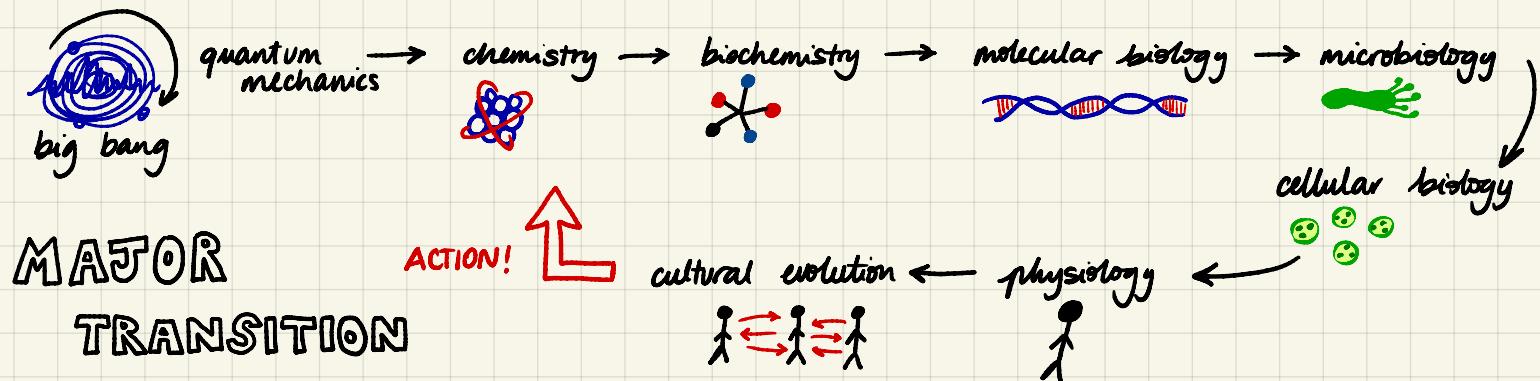
week one

con-silience: jumping together two different practices design & science
from theory to practice in biology and science → next week agronomy
and conservation

Nuria Conde - biology & computer science, multidisciplinary biologist.

complex systems → synthetic biology.

"Starting from zero" forget everything about Biology



WHAT IS ALIVE? a piece of information that is able to perpetuate itself

what about conscience? Dan Dennett

Crispr technology - Ctrl + C Ctrl + V of genetics
↳ Genetic therapy without high probability of cancer



Question becomes: WHAT SHOULD WE MODIFY?

- size?
- life span?
- replacements?
- new skills?

CANNOT PATENT GENES → open source

Alexandra Elbakyan: sci-hub, open source (illegal) platform for scientific papers.

PLANETARY WELLBEING

population growth = exponential

Element exhaustion: lithium, phosphorus ...

Contamination: microplastics, hormones ...

Global → Local: nuts, avocados, mosquitos ...

think globally, talk locally

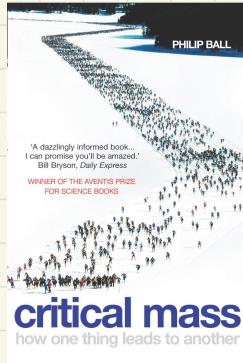
Climate refugees: people relocation due to climate change.

Hidden CO₂ impact: hard to understand impact

→ **Hidden Impact** - good book to read

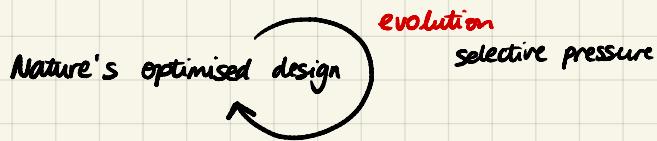
What we don't see - planned obsolescence

how many times do we have to reuse something to compensate CO₂ servers CO₂ emissions → streaming, 1MB = 7,072gr of CO₂



Replication of information
↳ Genes -
Memes -
Themes - technical replication of information

Evolution



= there are always constraints.

→ this means that evolution will always take place in similar ways.

come from different ancestors - but look / function the same.

{ GENETICALLY DIFFERENT
VISIBLY (PHENOTYPE) SIMILAR

symmetry is present everywhere - due to division of cells

Biomimicry - copying techniques used by nature.

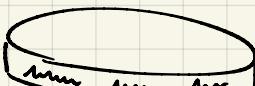
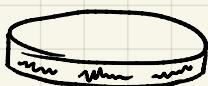
Biomimicry - copying techniques used by nature.

Mimicry / memristance - nature copying itself.

Accelerated directed Evolution

↳ compressing the amount of time for processes to take place
= SYNTHETIC BIOLOGY

CREATING ENVIRONMENTS FOR BACTERIA/FUNGI TO GROW



Mix together different ingredients to enhance growth of certain cultures.

MEDIUMS 1) Lactobacillus 2) Lactobacillus DIY 3) Yeast 4) Yeast DIY 5) All purpose

↓

- salt
- Bovine
- Agar powder

→ collecting samples for each medium

make sure the object (hand/spoon) is not going to contaminate or sterilize the sample.

↳ dirty
not sterile

↳ soap / alcohol
residue

SAMPLES

ALL PURPOSE MEDIUM

1) IAAC PUDDLE

and letting them dry

method: after sanitising my hands, I collected some mud from the puddle at the back of IAAC.

expectation: large growth of bacteria and/or fungi due to lack of water circulation
→ like swamp.

2) TATIANA'S SCALP

method: hand sanitised & dry, I scratched and rubbed my scalp then deposited residue on dish.

expectation: growth of bacteria typically present on human skin & membranes
→ maybe perfume / hair products affect?

LACTOBACILLUS

3) TATIANA'S EYE

method: hand sanitised & dry, I rubbed my inner eye and collected residue from eyelashes.

expectation: similar growth to scalp with variation of bacteria typically present in eyes.
→ maybe makeup / products residue?

BIO CHEMISTRY

All living things on earth require

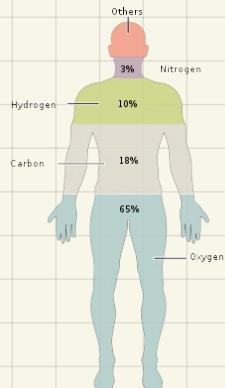
Hydrogen

Oxygen

Carbon

Nitrogen

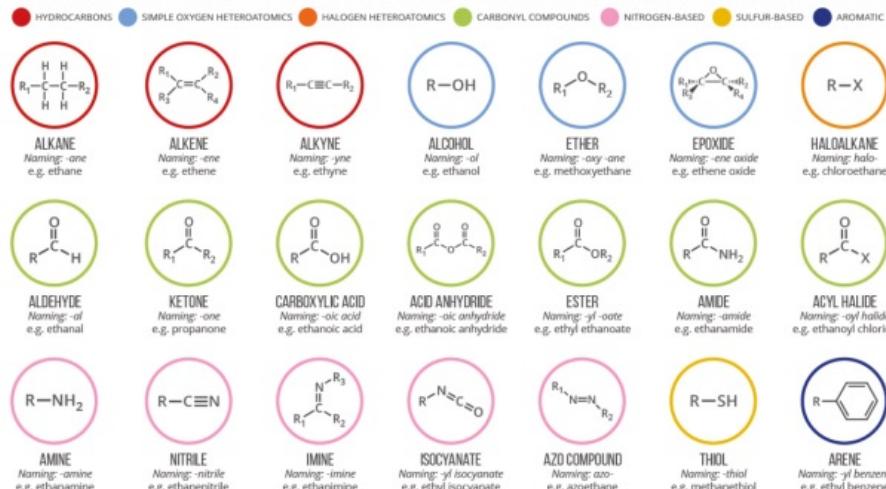
4 organic basic elements.



Functional groups are created by these 4 elements.

FUNCTIONAL GROUPS IN ORGANIC CHEMISTRY

FUNCTIONAL GROUPS ARE GROUPS OF ATOMS IN ORGANIC MOLECULES THAT ARE RESPONSIBLE FOR THE CHARACTERISTIC CHEMICAL REACTIONS OF THOSE MOLECULES. IN THE GENERAL FORMULAE SHOWN BELOW FOR EACH FUNCTIONAL GROUP, 'R' REPRESENTS THE REST OF THE MOLECULE, AND 'X' REPRESENTS ANY HALOGEN ATOM.

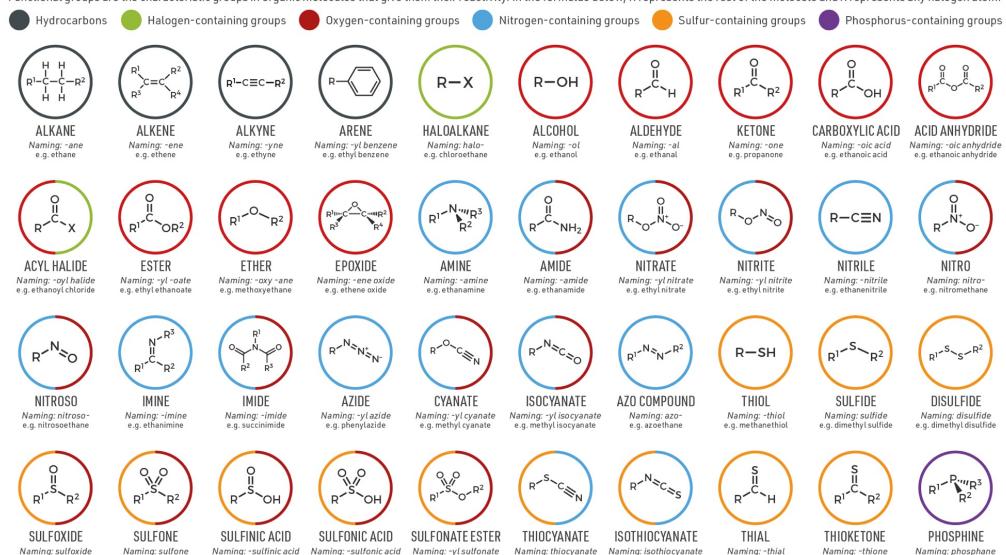


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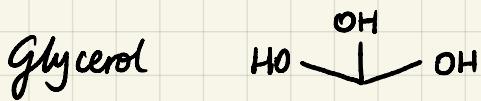
FUNCTIONAL GROUPS IN ORGANIC CHEMISTRY

Functional groups are the characteristic groups in organic molecules that give them their reactivity. In the formulae below, R represents the rest of the molecule and X represents any halogen atom.

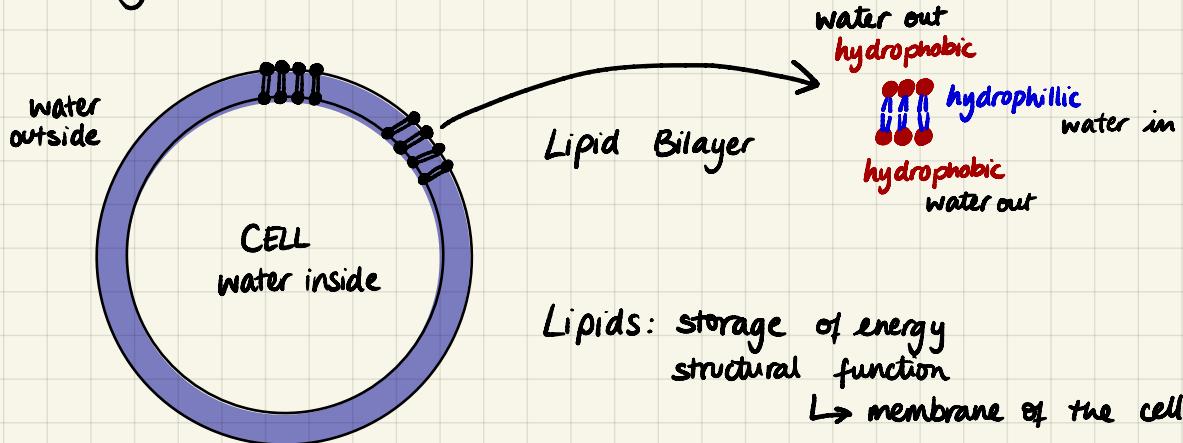


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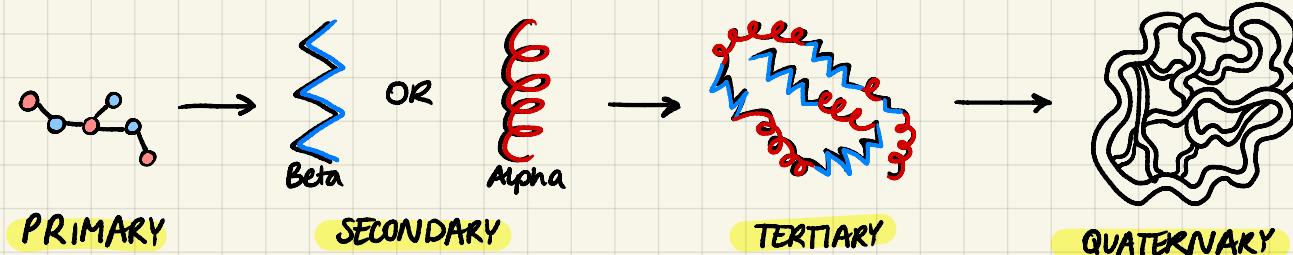
Fatty acids



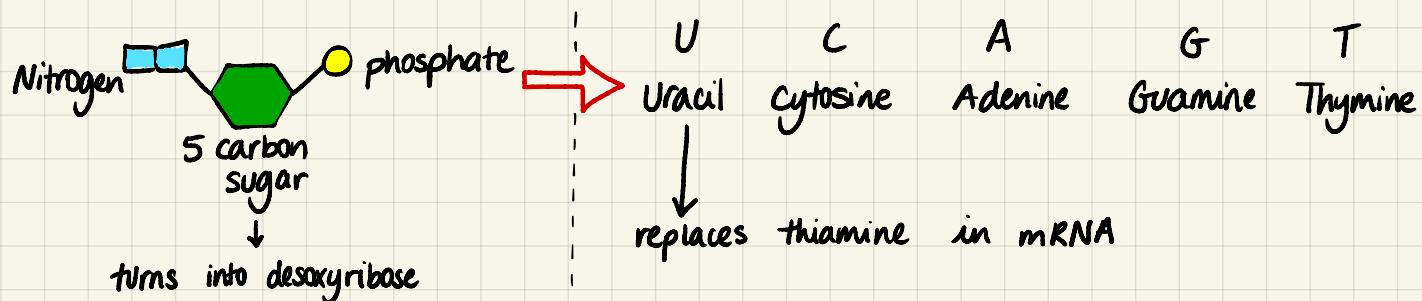
Lipids: storage of energy
structural function

→ membrane of the cells

Protein - chains of amino acids which take on different structures:



Nucleotides



ATP : Adenosine Triphosphate

the energy-carrying molecule used in cells because it releases energy quickly

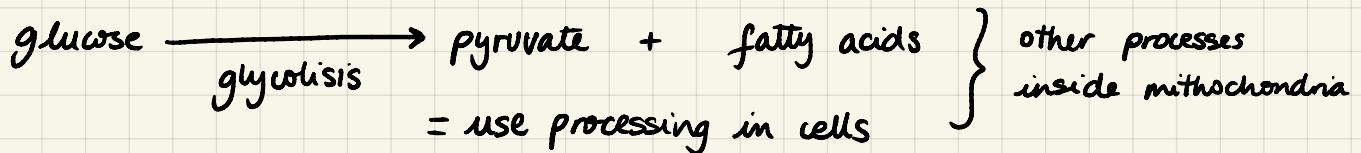
Enzymes: responsible for chemical reactions in body
= proteins ending in -ase

Metabolism: all the chemical reactions that take place in the cell.

- ↳ **Anabolism**: Building & bond making process that forms larger macromolecules
= requires energy
- ↳ **Catabolism**: Breaking down of molecules to make smaller ones
= releases energy

CATABOLISM : Aerobic respiration

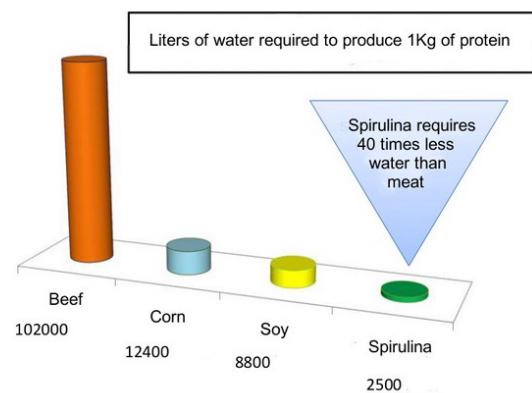
Glucose in → CO_2 out
+ Oxygen
+ Water



we need 9 enzymes for this transformation

SPIRULINA will solve all your problems

- low energy production
- high protein + nutrition value / gram
- can be made from pee



Spirulina: Growing

10L Medium

- 10L Water (no chlorine)
- 100gr Sodium bicarbonate
- 50gr Salt (NaCl)
- 200ml Macronutrients
- 10ml micronutrients

1L Macro Nutrients

Urine!
0.75 meat
1.5 vegan

- 1L de agua
- 100gr Potassium Nitrate
- 10gr Monoamonic Fosfate
- 5gr Potassium Sulfate
- 5gr Magnesium Sulfate

1L Micro Nutrients

- 100gr rosted iron nails
- 1L vinegar
-
- 10 gr Iron Sulfate
- 1L diluted vinegar/ G-tea

MICROBIOLOGY

the study of microscopic organisms (microbes)
↳ single cell (unicellular) or cell clusters.
includes fungi, protists & monera.

CLASSIFICATION - By nutrition

- Autotrophes - respiration, photosynthesis
= able to feed themselves

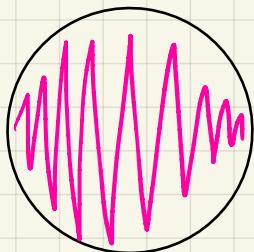
- Heterotrophes - require food to live

- By information

- Eukaryote - "after the membrane"

- Prokaryote - "before the membrane"

IDENTIFYING MICROORGANISMS



→ colony shape will vary

FORM

circular

irregular

filament

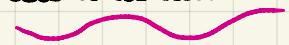


etc.

1) look for the colony shape

2) Microscopic observation

GRAM NEGATIVE



SANDWICH

GRAM POSITIVE

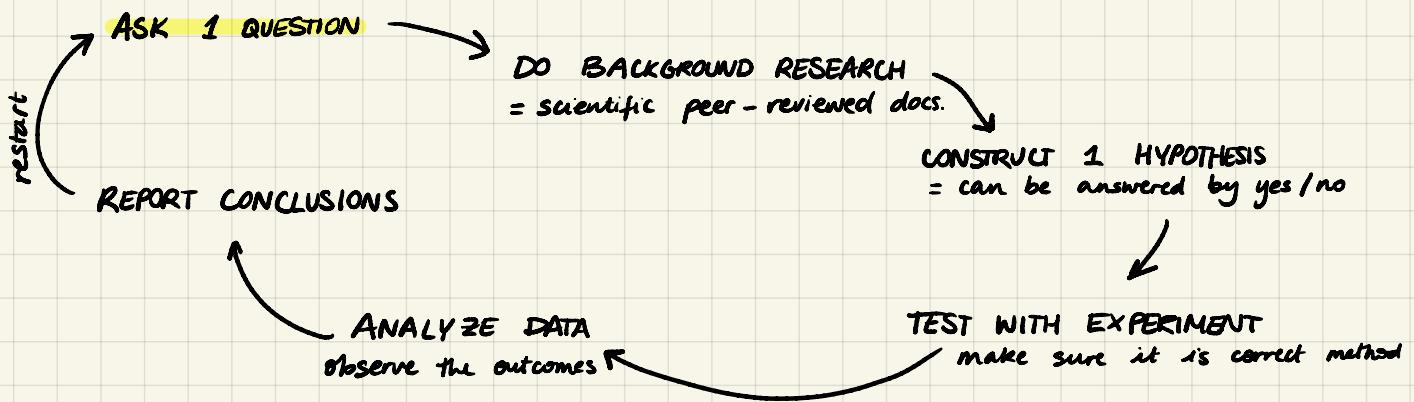


TOAST

the gut microbiome influences brain processes

our microbiome is an indication of our self.

The scientific method



Negative & positive controls

= have reference points

Negative yields 0 results, Positive yields desired result.

Assignment: Read a scientific paper + write summary of it & why it's important for future

Review

Upcycling and catalytic degradation of plastic wastes

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SUMMARY

Various recycling technologies have been developed to deal with plastic problems, but they face considerable economic and technological challenges in practice. An attractive alternative is upcycling, which aims to dig out the embedded value to incentivize large-scale valorization of plastic wastes. The degradation of nonrecoverable plastic wastes is another necessity to treat the omnipresent pollution. This review presents an overview on the conversion of plastic wastes toward value-added products and the catalytic degradation of nonrecoverable plastic wastes. Based on an examination of traditional recycling technologies and products, we summarize the state-of-the-art design and development of plastic conversion to high-value and high-performance fuels, chemicals, and materials. Subsequently, we highlight the advances in catalytic degradation of plastics to environmentally benign or degradable products and mineralization into carbon dioxide and water. We conclude with our perspective on the ongoing challenge and opportunities.

1 plastic conversion → fuel, chemicals, materials
2 catalysis of plastic !* → $H_2O + CO_2$

INTRODUCTION

Since the appearance of the first synthetic polymer in 1907, various plastics have been increasingly manufactured and used in ever-expanding fields because of their low cost, durability, safety, and processability.¹ Nowadays, plastics-based materials have become ubiquitous and indispensable in modern society, with a wide scope and range of applications that cannot currently be displaced by other materials.² Along with an excessive dependence on plastic products, the end-of-life treatment of post-consumer plastic wastes has become a huge problem because plastics are designed to be robust and durable. As of 2015, 6,300 Mt of plastic wastes had been cumulatively generated; of which, 79% entered landfills or accumulated in the natural environment, and 12% was incinerated.³ Only 9% of plastic wastes have been recycled, and most of the recycled plastic is down-cycled toward less-recyclable and low-value products, such as plant pots and garden furniture.^{4,5}

Because of this externality, global plastic pollution, as a planetary boundary threat, had already formed before people began to realize its enormity, complexity, and urgency.^{6,7} Plastic wastes are omnipresently and increasingly observed in oceans, lakes, rivers, soils, sediments, the atmosphere, and animal biomass.^{8–12} Microplastic (≤ 5 mm) and nanoplastic (≤ 100 nm) pollution originated from both direct emission of "microbeads" and "micro-exfoliates" (primary microplastics) contained in household cosmetic products into household wastewater and from the breakdown of larger plastic waste into small plastic pieces (secondary microplastics) via photooxidation under solar irradiation, physical crushing, and biodegradation in the natural environment.^{13–18} Microplastics and nanoplastics can be ingested by various organisms, and nanoplastics can even accumulate in plants,^{16,19} ultimately resulting in

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their enrichment via food webs. Plastic debris can function as a medium to compile and spread hydrophobic organic pollutants, heavy metals,²⁰ and diseases.²⁰ Although the direct toxicological effect of plastics on human health has not been substantiated, the ever-increasing emission of plastics is destined to generate multiple harmful effects.^{5,21} For example, microplastics have increasingly entered into the human food system, such as seafood,²² tea,²³ and vegetables,²¹ as a nonnegligible threat to food safety and agricultural sustainability.²⁴ Moreover, microplastics have been detected in human placentas.²⁵ In addition, global green house gas (GHG) emissions from the plastic life-cycle is expected to rise from 1.7 Gt of carbon dioxide (CO₂) equivalent in 2015 to 6.5 Gt in 2050 under current trends, contributing significantly to climate change.²⁶

The improper management of plastic wastes not only contaminates the environment but also signifies an immense loss of economic value.²⁷ Globally, the energy savings for plastic waste recycling are estimated to be 3.5 billion barrels of oil, equivalent to about \$176 billion dollars.²⁸ Although several recycling technologies have been investigated, they suffer universally from low benefits, high costs, and secondary pollution, leading to limited practical applications.²⁹ Therefore, the development of cost-effective, environmentally friendly, and efficient approaches to valorize plastic wastes into value-added products is indispensable to prevent their dissemination into natural environment. In addition, the development of effective catalytic-degradation technologies is essential for treating nonrecoverable plastic wastes.

We begin this review by providing a brief assessment on possible options to address the plastic problems. In combination with the development of recycling technologies, we summarize recent advances in upcycling to valuable chemicals, fuels, and materials. Then, we focus on the catalytic degradation of unrecoverable plastic wastes. We do not provide a comprehensive discussion on other related important aspects, such as traditional recycling technologies,^{28,30–32} biotechnological degradation,^{29,33} production of polymers from renewable resources,³⁴ and the development of recyclable and degradable polymers,^{35,36} because excellent reviews could be found elsewhere.

OPTIONS TO ADDRESS THE PLASTICS PROBLEM

Most plastic wastes fall into four top categories (Figure 1A): polyester, polyolefin, polyvinyl chloride (PVC), and polystyrene (PS).³⁷ Polyethylene terephthalate (PET) is the most widely used polyester, with a global annual production of 70 million tons (Mt) for use in textiles, packaging, carpeting, and single-use beverage bottles.^{38,39} Polyolefins, including polyethylene (PE) and polypropylene (PP), with annual production of approximately 138 and 80 Mt, respectively, account for 57% of the plastic content of municipal solid waste.^{3,40} Among PEs, high-density polyethylene (HDPE) is used extensively for electrical insulators, toys, bottles, pipes, and films, whereas low-density polyethylene (LDPE) is mainly used in devices, food packaging, and plastic wrap.²⁸ As the cheapest plastic, PVC is one of the most problematic wastes for the environment because of the emission of phthalate plasticizers and chlorine-containing hydrocarbons (dioxins) during its end-of-life treatment.³⁷ Detailed information on the production, properties, and application of other plastics can be found in previous reviews.^{28,41} Among the various plastic wastes, only PET and HDPE are routinely recycled, but the reclamation rate is far from satisfactory.³⁹

The 6R principle (reduction, repair, reuse, recover, remanufacturing, and recycling,⁴² with another version as rethink, refuse, reduce, reuse, recycle, and replace³³) of the

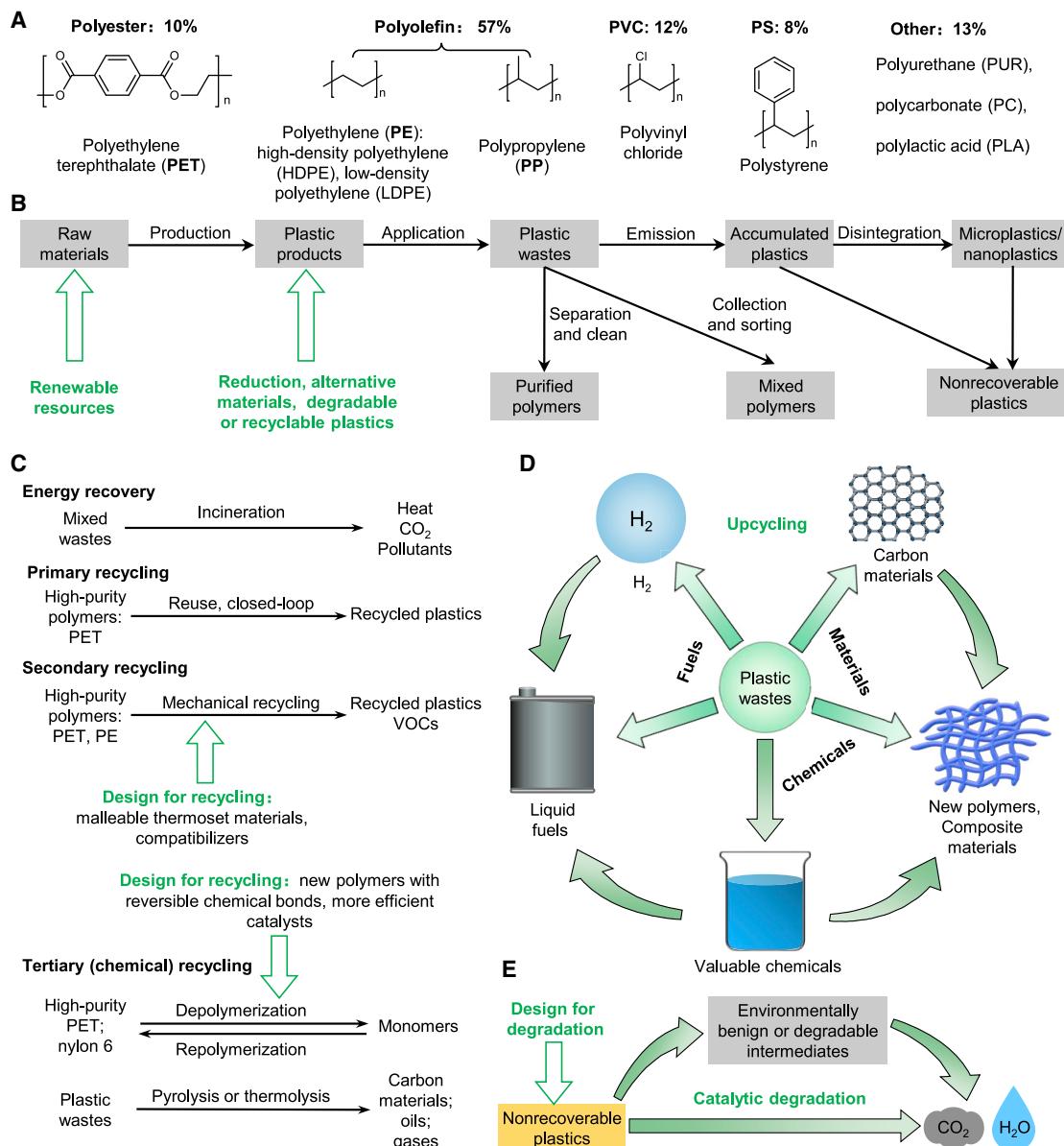


Figure 1. Options to address the plastic problems

- (A) Main types of plastic waste.
- (B) Process of plastic-waste generation.
- (C) Traditional recycling technologies.
- (D) Upcycling toward value-added products.
- (E) Degradation of plastic wastes.

circular economy offer a basic framework to seek solutions for the plastics problem. In principle, cutting down the use of plastic materials (reduction) and substituting alternative materials for the plastic (Figure 1B) would prevent the generation of plastic wastes and, in addition, relieve the excessive dependence on depletable resources. Despite considerable endeavors, currently, sophisticated plastic materials will continue to dominate for the long term, and many of them cannot be replaced with other materials because of the cost and the disparity in performance.^{43,44} For degradable and recyclable materials, it is difficult to concurrently satisfy the tough

requirements for material properties, cost, and degradability or recyclability. The design and development of degradable polymers, which undergo triggered degradation under environmentally authentic conditions once they are disposed of in the natural environment, must still guarantee long-term durability during shelf and service life, which is extremely challenging.³⁵ For instance, polylactic acid (PLA, also termed polylactide), one of most widely used degradable materials at present, is basically non-degradable in seawater.⁴⁵

Numerous recycling processes (Figure 1C), including primary (closed-loop) recycling, secondary (mechanical) recycling, tertiary (chemical) recycling, and incineration have been established to treat post-consumer plastic wastes. Both primary and secondary recycling are based on mechanical processes, including sorting, grinding, washing, remodeling, and extruding.²⁸ Primary recycling refers to processing of discarded plastic to make fresh products that are returned to the same or similar-quality applications. That process can only treat near-pristine plastic of a known origin.^{28,30} Secondary recycling refers to reprocessing of plastic wastes into products for uses that are different from the initial material through mechanical processes.²⁸ Because processing under harsh conditions (high temperature and mechanical force) unavoidably results in the degradation of polymers, the recovered low-grade plastics with inferior optical, thermal, and mechanical properties can only be employed in applications with less-engineering requirements than that of the original application⁴⁶, such that the mechanical recycling is also termed “downgrading” or “downcycling.”²⁸ Currently, mechanical recycling is only used commercially for the recovery of PET and PE.²⁷ The ultimate fate of mechanically recovered plastic products is still landfilling, disposal, or incineration because of performance deterioration of the regenerated materials.¹ In addition, the mechanical recycling processes usually emit several volatile organic compounds.⁴⁷

Tertiary recycling refers to recycling of plastics through chemical routes, such as pyrolysis, gasification, and depolymerization.²⁸ Pyrolysis (also called thermolysis, thermal cracking, catalytic cracking, and liquefaction) converts plastics to gases, liquids, and waxes under high temperatures, either in the absence of a catalyst or in the presence of a catalyst (catalytic pyrolysis).³¹ Gasification aims to produce gas products under high temperatures with a gasification agent, such as air or oxygen.⁴⁸ Because the polymeric molecules of the plastic typically have a high molecular weight (5,000–5,000,000 g mol⁻¹) with robust chemical bonds, their degradation into a myriad of small molecules via multiple side reactions seems to be inevitable in traditional pyrolysis processes, resulting in poor control of the reaction pathway and low selectivity for desirable products.⁴⁹ Avoiding side reactions and narrowing product distributions are fundamentally important for traditional pyrolysis processes. Depolymerization refers to converting the polymers to well-defined monomers or oligomers via the disruption of certain chemical bonds.³¹ For a detailed discussion of these process descriptions, the reader is referred to a more specialized review.³¹ Chemical recycling is ill-suited for many kinds of plastic wastes that are composed of robust chemical linkage, such as polyolefins.⁴³ Even for polymers with tractable chemical bonds, the recovery of monomers from plastic wastes is often costly, energy intensive, and incompatible with complex mixtures.⁵⁰ Because real-world plastic wastes generally contain plasticizers, inks, dyes, and adhesives³⁹ and are mixed with other polymers or contaminated by other wastes, chemical recycling requires time- and energy-consuming separation and purification steps, thus leading to a further decrease in overall economic feasibility or resulting in reduced performance of the regenerated products.

In comparison with recycling technologies, incineration is a more all-purpose technology, which has been routinely employed for end-life treatment of mixed or contaminated wastes at sizable scales. Although incineration can recover partial energy in the form of heat from mixed wastes without the need for separation, it is an unfavorable process in view of the overall energy loss relative to recycling,⁵¹ high GHG emissions (5 to 10 tons of CO₂ per ton of plastic during the entire life cycle),³¹ and toxic combustion products.^{26,52}

Frustratingly, the above strategies cannot end the environmental crisis associated with anthropogenic plastics. A state-of-the-art scenario analysis shows that implementing the most aggressive solutions from 2016 to 2040 through the use of currently available knowledge and technologies, including collection, disposition, recycling, reduction, and substitution could reduce plastic pollution by 40% relative to 2016, but 710 Mts of plastic waste will still be discharged inescapably into aquatic and terrestrial ecosystems, accompanied by the emission of large quantities of GHGs from plastic manufacturing and unsound waste-management activities.⁸ Therefore, extraordinary efforts are indispensable to achieve a substantial reduction in global plastic emissions.⁵³

To overcome the inherent defect of conventional strategies, upcycling, which emphasizes the exploration of an inherent value in plastic wastes (Figure 1D), has been developed as a complementary and more attractive option.^{39,54} Until recently, there has not been an accurate definition of the concept of "upcycling." The terms "recycling" and "upcycling" have been used indiscriminately in some publications because some routes do have some overlaps and many upcycling processes are developed based on recycling processes. Comparatively, the former emphasizes "closed-loop" for the plastic materials themselves, whereas the latter will be an open-loop processes toward multiple profit streams. In this review, we define upcycling as the conversion of low-cost and abundant plastic wastes into high-performance fuels, chemicals, and materials via digging out the embedded value present in the form of carbon, hydrogen, chemical, energy, or macromolecular structure. Ideal, sustainable, or circular plastic-waste refineries⁵⁵ may be established to afford fuels, chemicals, and materials, similar to the well-applied oil refinery and preliminarily established biorefinery roadmap.⁵⁶ Moreover, upcycling processes may provide new approaches to handle real-world plastic wastes, in particular. those cannot be subjected to thermomechanical recycling. Therefore, there is no doubt that upcycling of plastic waste would simultaneously contribute to the mitigation of solid waste contamination and to the production of high-value products, hence, signifying considerable economic and scientific opportunities.⁵⁷

Both recycling and upcycling are designed for the valorization of post-consumer plastic wastes to prevent the emission of plastic wastes into the natural environment, but they cannot deal with nonrecoverable plastic wastes. In fact, there are vast and diverse plastic wastes that cannot be collected and used under current economic and technical condition, such as plastic fragments mixed with sludge and plastic debris dispersed in the natural environment. Commercially, running-water treatment technologies can remove microplastics from wastewater via skimming, sedimentation, and tertiary filtration, but most plastics without substantial degradation are still retained in sewage sludge.^{58–60} Environmental degradation of plastic wastes, including abiotic degradation and biodegradation behaviors, depends on many complex factors, including physical properties and molecular structures,^{61,62} and generally suffers from low efficiency.⁶³ Because of the strong chemical inertness of plastic wastes, natural degradation can take decades and continue to emit

hazardous organic pollutants during that time.^{64,65} Successful enzymatic or microbial degradation has largely concentrated upon a few types of plastic that contain hydrolyzable bonds.³³ Although considerable achievement has been reported on biotechnological degradation, its effectiveness under natural conditions remains to be validated.³³ Therefore, the development of effective catalytic degradation technologies, which could completely mineralize nonrecoverable plastic waste into CO₂ and water or degrade them to environmentally benign or degradable intermediates (Figure 1E), is of high importance for the remediation of plastic pollution.

UPCYCLING TO CHEMICALS

Catalytic depolymerization to monomers

Catalytic depolymerization to monomers, which is also termed chemical recycling to monomer,³¹ is an important form of chemical recycling.³⁰ It is different from mechanical recycling because the catalytic depolymerization of initial monomers enables the production of recovered plastic with properties that are the same as virgin plastic, if purified monomers can be obtained.³⁹ Under the framework of upcycling, both monomers and partially deconstructed polymers are important feedstocks for the development of new processes toward value-added chemicals, fuels, and materials. Catalytic depolymerization to monomers relies heavily on the presence of fragile chemical bonds in the skeleton of the polymers. At present, catalytic depolymerization to monomers predominantly concentrates upon polyesters, in particular PET, because the chemolysis of esters is relatively facile.

Various catalytic depolymerization methods have been investigated for the conversion of PET to monomers. The primary processes include hydrolysis with water to terephthalic acid (TPA) and to ethylene glycol (EG) under neutral, acidic, or basic conditions (Figure 2A); alcoholysis with alcohol (methanol, ethanol, etc.) to dialkyl terephthalate and EG; glycolysis with excess glycols (such as EG, diethylene glycol [DEG], propylene glycol [PG], polyethylene glycol, 1,4-butanediol, and hexylene glycol) toward bis(hydroxylethylene) terephthalate (BHET or other corresponding esters) via a transesterification reaction; and aminolysis with amines (or ammonolysis with ammonia) toward corresponding diamides of TPA and EG,^{66,67} among which, some depolymerization processes are also termed solvolysis.³¹ The reader can find systematic summaries of these processes in specialized reviews mentioned above. These methods can also be used for the depolymerization of other polyester plastics, such as polybutylene terephthalate (PBT).⁶⁸ Glycolysis is also the predominant catalytic depolymerization method for polyurethanes (PUR).⁶⁹ The harsh reaction conditions, the use of excess solvents and depolymerizing agents, as well as the formation of by-products are the main obstacles to commercial deployment of these processes.

Catalytic depolymerization back to the original monomers is rather difficult for many extant plastics, which are composed of robust chemical linkages because of the absence of fragile chemical bonds. For example, prohibitive amounts of energy are required to depolymerize polyolefins, such as PE and PP, to their original monomer subunits, along with low selectivity.⁴³ Similarly, pyrolysis of PS usually generates complex products with low selectivity.⁷⁵ Among polyamides (PAs), only nylon-6, which is synthesized from the seven-membered ring ϵ -caprolactam, is suitable for depolymerization back to monomers with relatively high yield and selectivity.³⁰ The depolymerization of most polyethers is difficult because of the challenge of activating unstrained ethers, whereas poly(tetrahydrofuran), an amorphous soft material widely used as a synthetic component in various industrial and consumer applications, is relatively amenable to catalytic depolymerization.⁷⁶

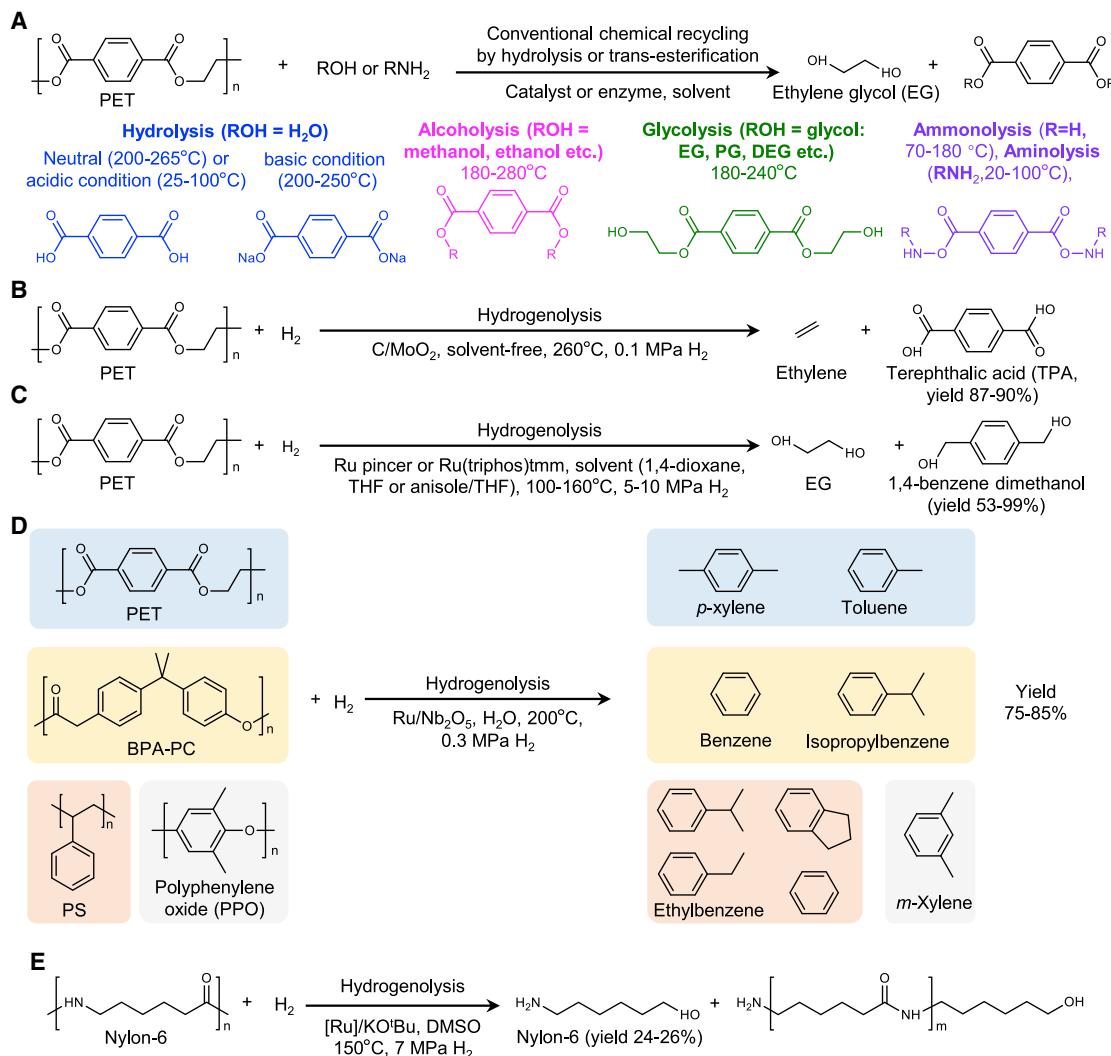


Figure 2. Catalytic depolymerization of plastics to monomers

- (A) Depolymerization of PET via hydrolysis or trans-esterification.⁶⁶
- (B and C) Hydrogenolysis of PET over (B) C/MoO₂⁴⁶ and (C) Ru catalysts.⁷⁰⁻⁷²
- (D) Hydrogenolysis of aromatic plastics over a Ru/Nb₂O₅ catalyst.⁷³
- (E) Hydrogenolysis of PET using a [Ru]/KO^tBu catalyst with dimethyl sulfoxide (DMSO) as the solvent.⁷⁴

Similarly, biotechnology offers promising paths for the depolymerization of polymers to well-defined oligomers or monomers for recycling and upcycling but is also limited to the few plastics with hydrolyzable esters or amides bonds, such as PET, PA, and selected types of PUR.³³ Recently, enzymatic hydrolysis achieved remarkable progress: for instance, the engineered PET depolymerase, which is obtained by computer-aided enzyme engineering, has afforded 100% PET conversion within 10 h, with a PTA productivity as high as 16.7 g L⁻¹ h⁻¹.³⁸ Another study shows that nanoscopically dispersing enzymes into polyesters during their production could greatly improve substrate accessibility, thus, allowing near-complete depolymerization of polyesters.⁷⁷

Catalytic hydrogenolysis to chemicals

Hydrogenolysis, a specific form of depolymerization, refers to disrupting chemical bonds, in particular, C–C bonds, with the assistance of hydrogen (H₂).³¹ In some

cases, plastics can be selectively deconstructed through hydrogenolysis to short-chain products with values that are substantially higher than the fully deconstructed monomers.⁴⁴ At present, upcycling of plastic wastes to value-added chemicals via direct hydrogenolysis mainly concentrates on PET and PE. Compared with the depolymerization processes based on hydrolysis or transesterification, catalytic hydrogenolysis has offered more accessible and promising options for the conversion of PET wastes to valuable chemicals and the drop-in integration of plastic valorization with well-established industrial processes toward an ideal circular economy. The use of the carbon-supported single-site molybdenum-dioxo (C/MoO₂) catalyst enables selective depolymerization of PET to TPA and ethylene (Figure 2B) under solvent-less conditions at 260°C in the presence of 1 atmosphere of H₂,⁴⁶ which is rarely achieved in traditional chemical and biological depolymerization processes. The reaction over C/MoO₂ catalyst proceeds via retro-hydroalkoxylation/β-C–O scission, followed by hydrogenolysis of vinyl benzoate. Moreover, high TPA yields are also obtained from waste beverage-bottle PET and PET/PP mixtures (simulation of bottle and cap, respectively), and the catalyst is recyclable without losing activity.

Selective hydrogenolysis of PET to 1,4-benzene dimethanol and EG (Figure 2C) under mild temperatures has been achieved over a series of ruthenium (Ru)-based molecular catalysts,^{71,72} using anisole, tetrahydrofuran (THF), or their mixture as solvent. These molecular catalysts are also capable of selectively depolymerizing PLA, polycaprolactone (PCL), poly(bisphenol A carbonate) (also termed bisphenol A polycarbonate [BPA-PC]), and PBT to the corresponding diols.⁷² The large-scale application of expensive, air-sensitive, potentially toxic Ru catalysts with complex ligands is unrealistic because of the difficulty of catalyst recycling, despite their high activity and selectivity.⁴⁶

Converting PET back to *p*-xylene and methylbenzene (Figure 2D) has been achieved via catalytic hydrogenolysis over a Ru/Nb₂O₅ catalyst in water.⁷³ This catalytic system also enables the hydrogenolysis of other aromatic plastic wastes with interunit C–O and/or C–C linkages toward arenes (75%–85% yield), including PS, poly(*p*-phenylene oxide) (PPO), BPA-PC, and mixed aromatic plastic wastes. In contrast, Pd- and Pt-based catalysts convert PET to ring-saturated products, whereas Ru/ZrO₂, Ru/TiO₂, and Ru/HZSM-5 catalysts convert PET to mixtures ranging from arenes to ring-saturated products with low selectivity. Compared with other catalysts, the Ru/Nb₂O₅ catalyst is selective in tailoring the C–O bond and the sp²–sp³ bond, that is, C_{aromatic}–C connected with aromatic rings, without hydrogenating aromatic ring, because of the presence of sub-nano Ru clusters and Lewis/Brønsted acid sites on Nb₂O₅. When treating mixed plastics, the Ru/Nb₂O₅ catalyst loses some activity (~28%) in the second run because of carbon deposition, but it is restored completely after calcination in air, followed by reduction with H₂.

Catalytic hydrogenation of robust PAs is difficult because they are resistant to most solvents because of the multiple, strong intermolecular hydrogen bonding interactions within the polymer chains. Hydrogenative depolymerization of nylon-6 to amino alcohols (Figure 2E) has been achieved by a combination of a ruthenium pincer ([Ru]/KO^tBu) catalyst in DMSO.⁷⁴ The use of DMSO as a solvent is crucial to disrupt hydrogen bonding and, in addition, to maintain the uncoordinated state of the metal center, whereas metal-ligand cooperativity is important for the hydrogenation of amide bonds through an outer-sphere mechanism. This catalytic system can also catalyze the hydrogenation of PUR to diol, diamine, and methanol. The diol and diamine can be used to produce original PA through a dehydrogenative coupling process using the same Ru catalyst, providing a potential route for the recycling of nylons.

PET, except for H₂, silanes have also been investigated for reductive depolymerization of plastic wastes. For example, PLA, PCL, and PBT can be successfully converted into value-added compounds, including *p*-xylene, 1,2-propanediol, 1,6-hexanediol, and THF, with a Zn(OAc)₂ · 2H₂O catalyst using (EtO)₂MeSiH or PhSiH₃ as the reductant.⁷⁸ The advantages of this catalytic system are its low cost and the good reusability of the catalyst, but silanes are very expensive.

Other routes to useful chemicals

Direct hydrogenolysis of polyolefins, including PE and PP, generally produce mixed alkanes with a wide molecular distribution, instead of well-defined monomers, even when elaborately designed catalytic systems are used, as will be discussed in the section of upcycling to fuels. The consumption of expensive H₂, which essentially originates from non-renewable fossil fuel resources, is a primary barrier to the application of hydrogenolysis technologies. Tandem catalysis, which refers to integrating multiple reaction steps into one-pot catalytic systems in an appropriate sequence through precise regulation of active sites, the chemical environment, and the reaction conditions, offers a promising strategy to inhibit unwanted side reactions to tailor a reaction pathway and then achieve selective, efficient conversion of plastic waste to target products. Recently, upcycling of PE to long-chain alkylaromatics (Figure 3A) has been achieved by tandem hydrogenolysis/aromatization over a commonly used heterogeneous catalyst, platinum nanoparticles supported on γ -alumina (Pt/Al₂O₃), without consuming the external hydrogen.⁴³ In contrast to pyrolysis, which generates complex, low-value mixtures under harsh condition (>400°C), the tandem catalytic system produces high yields (up to 80 wt%) of low-molecular-weight liquid/wax products with high selectivity for valuable long-chain alkylaromatics and alkyl-naphthalenes (average carbon atom number of ~30, dispersity [D] = 1.1) from various PE grades under solvent-less conditions at a moderate temperature (280°C). The conversion of two commercial-grade PE samples with higher-molecular-weight, LDPE plastic bag and HDPE water-bottle caps produces overall liquid yields of 69 wt% and 55 wt% with alkylaromatic selectivities of ~44 mol% and 50 mol%, respectively, validating its applicability to real-world plastic wastes. During the reaction, hydrogenolysis of PE chains can consume H₂ and then reduce the thermodynamic values (ΔG and ΔH) of aromatization, whereas aromatization generates H₂ to induce the hydrogenolysis (Figure 3B). The liquid alkylaromatics can be used as feedstocks to produce various products of daily life, such as surfactants, lubricants, refrigeration fluids, and insulating oils. In addition, theoretical simulation suggests that the tandem olefin metathesis and double-bond isomerization may selectively convert PE waste with excess ethylene into propylene products that are worth about \$0.20~0.30/mol higher than an ethylene feedstock.⁷⁹

Taking advantage of existing refinery technology and infrastructure is crucial to exploring effective recycling and upcycling routes. For instance, the refinery-waste catalyst, which is discarded as waste during the industrial-fluid catalytic-cracking process is employed to convert PP, and the same aromatics content is obtained with fresh catalyst with considerably inhibited coke deposition.⁸¹ The improved aromatization and pre-cracking activity is attributed to the deposition of Fe, Ni, and V onto the catalyst during the fluid catalytic cracking. Meanwhile, the lifetime of the catalyst is improved because of the decreased coke deposition, which is attributed to the block of micropore structure in the zeolite material as well as to the absence of acid sites.

A tandem-catalysis strategy has also been successfully used for the conversion of PET to benzene, *p*-xylene, and methylbenzene (BTX) without using external

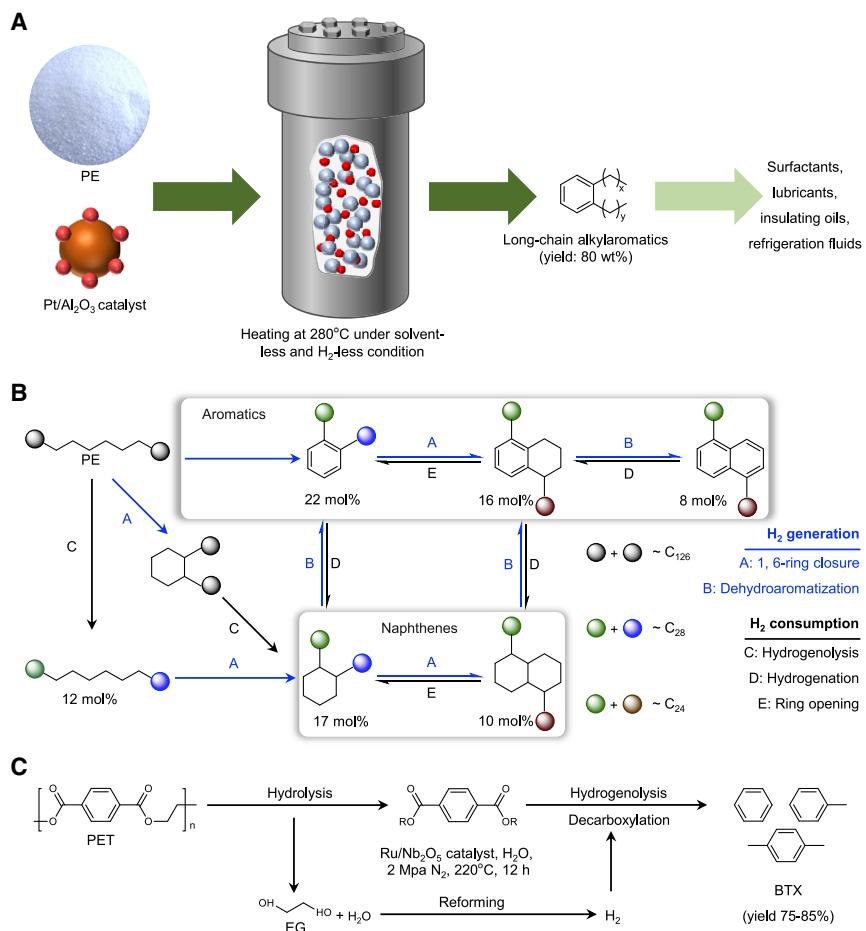


Figure 3. Upcycling of PE and PET through a strategy of tandem catalysis

(A and B) Schematic illustration of PE upcycling to long-chain alkylaromatics via tandem hydrogenolysis/aromatization (A) and a reaction pathway and mechanism for the conversion of PE to alkylaromatics and alkylnaphthenes (B).^{43,57} (A) was adapted with permissions,⁵⁷ copyright 2020, AAAS.

(C) H₂-free conversion of PET to arenes.⁸⁰

hydrogen sources (Figure 3C), as an alternative approach to hydrogenolysis.⁸⁰ Compared with the hydrogenolysis of PET over a Ru/Nb₂O₅ catalyst at 200°C in the presence of 0.3 MPa H₂, H₂-free conversion of PET back to BTX in the same catalytic system was achieved by unearthing hidden structural hydrogen under relatively harsh reaction conditions (220°C), affording total monomer yields up to 91.3% with quantitative selectivity to BTX (>99.9%). The Ru/Nb₂O₅ catalyst could catalyze three tandem steps, including PET hydrolysis, EG reforming to H₂, and hydrogenolysis of C–O/C–C bonds, along with partial decarboxylation reaction.

The application of other catalytic technologies in plastics upcycling may also produce useful products. For example, PE waste can be used to synthesize plasticizers for PLA.⁸² Under microwave radiation, both HDPE and LDPE are selectively oxidized by HNO₃ to dicarboxylic acid mixtures, including succinic, glutaric, and adipic acid.^{82,83} The reaction of dicarboxylic acid mixtures with 1,4-butanediol and crotonic acid delivers plasticizers. The resulting plasticizers can be covalently attached to PLA by a reactive extrusion process, improving the strain at break to 142% and decreasing the glass-transition temperature by 10°C. The integrated processing of

polyoxymethylene polymer waste with biomass-derived diols, such as 1,3-propane-diol over an acid catalyst, affords cyclic acetals as promising solvents, fuel additives, pharmaceutical intermediates, and polymeric monomers.⁸⁴

UPCYCLING TO FUELS

The elementary compositions of many plastics, in particular the C and H content in polyolefins are close to petroleum-derived hydrocarbons. As a consequence, the calorific values of plastic wastes are comparable to currently used liquid fuels.⁸⁵ In addition, plastic wastes are also considered as alternative hydrogen-rich energy feedstock because of the relatively high hydrogen content (approximately 8–14 wt %).⁴⁹ Although pyrolysis and gasification have been extensively investigated to convert plastic wastes to fuels, they yield only complicated mixtures, which require tedious separation, purification, and upgrading process to provide commercial fuel products. In contrast, upcycling to high-performance fuels, including H₂ and liquid alkanes with a narrow molecular-weight distribution has shown great promise for the valorization of plastic wastes.

Hydrogen

Photoreforming is a solar-driven technology that uses the energy of sunlight to convert organics and water to value-added products, such as H₂ and small organic molecules.⁸⁶ Most research on photocatalytic H₂ production is based on the decomposition of an unrealistic sacrificial agent, such as triethanolamine into H₂, instead of overall water splitting, whereas earlier photoreforming of organic waste universally focuses on simple “model waste” substrates, such as ethanol, glycerol, or soluble sugars. For many common organic wastes, the overall photoreforming process is nearly energetically neutral and more favorable than water splitting.⁸⁶ Therefore, photoreforming has provided a promising approach to simultaneously deal with organic solid wastes and energy challenges with the reduction of anthropogenic GHG emissions.⁸⁷ Generally, the photoreforming of hydrocarbon-chain-based plastics (non-polar polymers), is challenging because of the difficulty of breaking down highly stable C–C bonds,⁸⁶ despite the relatively high hydrogen content. In contrast, the plastics that contain oxygenated, polar groups or esters (polar polymers), such as PET, PUR, and PLA, are more amendable feedstocks.

The photoreforming of actual plastic was first attempted in 1981 using platinized TiO₂ as a photocatalyst in an NaOH aqueous solution (5 M), with low H₂ evolution rates.⁸⁸ The visible-light-driven, noble, metal-free photoreforming of plastic has been achieved by combining CdS/CdO_x quantum dot catalyst with 10 M NaOH solution (Figure 4). This catalytic system attains maximal H₂ production rates of 64.3 ± 14.7, 3.42 ± 0.87, and 0.85 ± 0.28 mmol H₂ g_{CdS}⁻¹ h⁻¹ from PLA, PET, and PUR, respectively.⁸⁹ When using realistic PET water bottle as the feedstock, it still affords H₂ production rates of 4.13 ± 0.40 mmol H₂ g_{CdS}⁻¹ h⁻¹ with a rate of conversion of 5.15% ± 0.72% and an external quantum yield of 2.17% ± 0.38%. The superior catalytic performance of CdS/CdO_x is attributed to the excellent visible light absorption ability, high dispersity, and high activity under strong alkaline condition as well as the partial dissolution and hydrolysis of plastics to monomers induced by NaOH. The strong alkaline condition leads to the *in situ* formation of thin oxide/hydroxide layer on the surface of CdS, which could not only prevent the photocorrosion of CdS but also improve the photocatalytic activity.⁹⁰ However, the H₂ cannot be completely released, and the overall conversion does not outperform 40%, with the formation of organic molecules, such as formate, acetate, and pyruvate, which undergo slow photoreforming.

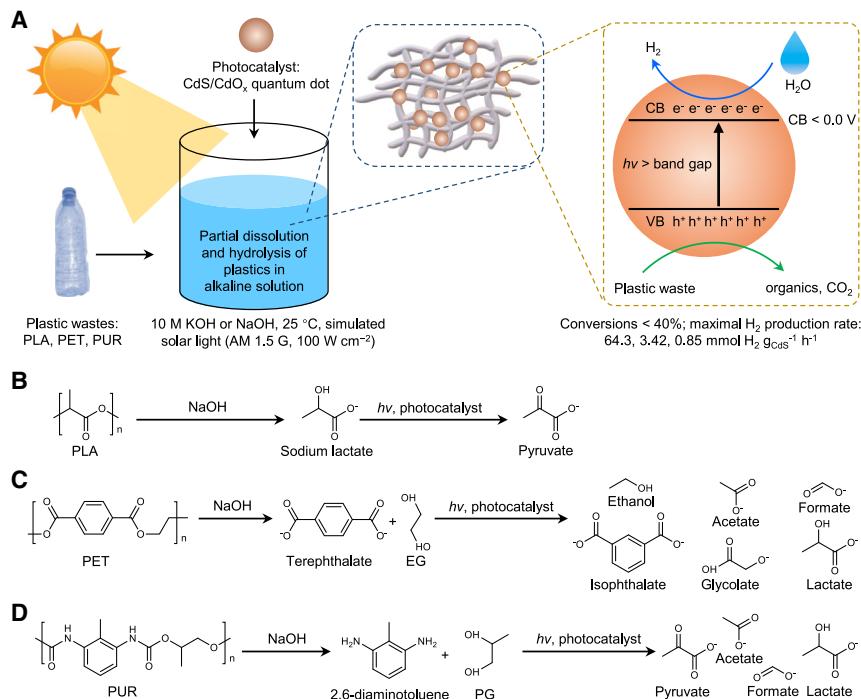


Figure 4. Photoreforming of plastics to H₂

(A) Schematic illustration of the photoreforming process of plastics over a CdS/CdO_x quantum-dot photocatalyst in an alkaline aqueous solution.⁸⁹ Adapted with permissions,⁸⁹ copyright 2018, Royal Society of Chemistry.

(B–D) Conversion of PLA (B), PET (C), and PUR (D) to organic products.⁸⁹

To displace the noble metal and Cd-based catalysts, cheap and nontoxic carbon nitride has been investigated for photoreforming.⁹¹ After pretreatment with an NaOH solution (stirring at 40°C in the dark for 24 h), 72% of PLA is converted to lactate, whereas 62% of EG is released from PET. The cyanamide-functionalized carbon nitride (CN_x) coupled with a nickel phosphide (Ni₂P) provides two and four times less H₂ yield than those with CdS/CdO_x for PLA and PET, respectively, with oxidation products similar to those over CdS/CdO_x. The additional electron-transfer process from the light absorber CN_x to the cocatalyst Ni₂P is one of the main limiting factor for the activity. The catalytic system can convert microplastics (polyester microfibers) and food-contaminated plastic without compromising catalytic activity when the reactor is upscaled from 2 to 120 mL.

These photoreforming studies represent useful proofs-of-concept, but their application faces a series of economic and technologic hurdles. It is estimated that the economically and environmentally feasible running of photoreforming requires a 50 times greater H₂ evolution rate ($>0.004 \text{ mol H}_2 \text{ g}_{\text{substrate}}^{-1} \text{ h}^{-1}$, conversion of $>50\%$ per day, and external quantum yield of $>50\%$) and greater durability of the photocatalyst (lifetime > 1 year).⁸⁶ Currently, the knowledge of the mechanism of oxidation half-reaction, the rate-limiting step for photoreforming, is still limited, and the selective oxidation of plastic to value-added chemicals has not been proven. Strong alkaline conditions are crucial for partial solubilization and hydrolysis of solid feedstock both in pretreatment and photoreforming processes and can greatly improve photoreforming efficiency. However, large-scale use of alkaline solution is not viable in terms of both cost and energy returned on energy invested, even assuming it can be recycled 60 times. The design of more-efficient and stable

photocatalysts and co-catalysts, the improvement of substrate-catalyst contact, the screening of suitable solvent,⁹² the development of pretreatment methods, and an examination of useful oxidation products are needed to promote the establishment of economically, environmentally, or energetically favorable photoreforming processes.

Selective, rapid, and one-step upcycling of real-world plastic wastes, including milk containers (HDPE), plastic bags (LDPE), food wraps (PP), and plastic foam (PS) to high purity H₂ and high-value carbon materials, predominantly in the form of multiwalled carbon nanotubes (MWCNTs) has been achieved by microwave-initiated catalytic deconstruction.⁴⁹ Composite iron oxide and aluminum oxide (FeAlO_x) functions as both the microwave susceptor and the catalyst to initiate a rapid conversion of plastics under solvent-less conditions, obtaining excellent H₂ yields of 55.6, 51.4, and 26.9 mmol g_{plastic}⁻¹ from mechanical, pulverized HDPE, PP, and PS (theoretical yield, 71.4, 71.4, and 38.4 mmol g_{plastic}⁻¹), with negligible liquid and carbon yield up to 0.70, 0.60, and 0.80 g · g_{plastic}⁻¹, respectively. Combined with other gas products, near-quantitative hydrogen (97%) has been extracted within 90 s. In contrast, both the use of carbon materials as a catalyst under microwave conditions and the use of FeAlO_x as the catalyst in traditional pyrolysis processes produce low H₂ yields. The effective conversion is due to the following reaction mechanism: (1) the selective generation of heat over the catalyst; (2) heat is transferred from the catalyst to the plastic; (3) the microwave initiates the scission of the C–H bonds over the catalyst, forming H₂ and carbon; (4) and the partial-carbon species reacts with the FeAlO_x to form Fe₃C, which assists in the generation of the MWCNTs. Unlike conventional heating processes, the preferential heating of the catalyst could promote the desorption of hydrogen from active sites and avoid fundamental side reactions, thus leading to the selective conversion of plastics toward target products.

Alkanes

Catalytic hydrogenolysis can convert PE and PP into alkane products, including lubricants, waxes, diesels, and light-hydrocarbon gases, but these processes generally suffer from a lack of product control and consumption of expensive H₂.^{93,94} Recently, upcycling of HDPE toward diesel and lubricant-range alkanes with high yield (79%) and narrow distribution (from C₉ to C₁₈) has been achieved over an ordered, mesoporous shell/active site/core catalyst (mSiO₂/Pt/SiO₂), a chemically and thermally robust inorganic material.⁴⁴ In contrast, the Pt nanoparticles supported on silica spheres (Pt/SiO₂) without a mesoporous SiO₂ shell broke HDPE chains randomly toward alkane products with wide carbon chain distributions and lower yields (52.8%). Selective hydrogenolysis is preceded by a processive mechanism that resembles enzyme-catalyzed depolymerization of biomacromolecules to atom-precise fragments. The long PE chains readily enter the nanopores and are then bound at a desired position via polymer-surface interactions. Subsequently, the Pt nanoparticles selectively cleave the C–C bond in the PE at regular intervals. Finally, small-molecule products are desorbed and released because of the weak interaction between the small molecules and the catalyst.

As described in the section of other routes to useful chemicals, tandem catalysis has provided an effective strategy for the upcycling of PE and PET to value-added chemicals without consuming external hydrogen. Tandem catalytic cross-alkane metathesis (CAM) using low-value and widely available short alkanes (Figure 5) as cross-metathesis partners enables the efficient conversion of different types of PE to liquid fuels and waxes under relatively mild conditions (175°C).⁴⁰ During the reaction, the iridium (Ir) complex catalyzes the dehydrogenation of both PE and short alkane,

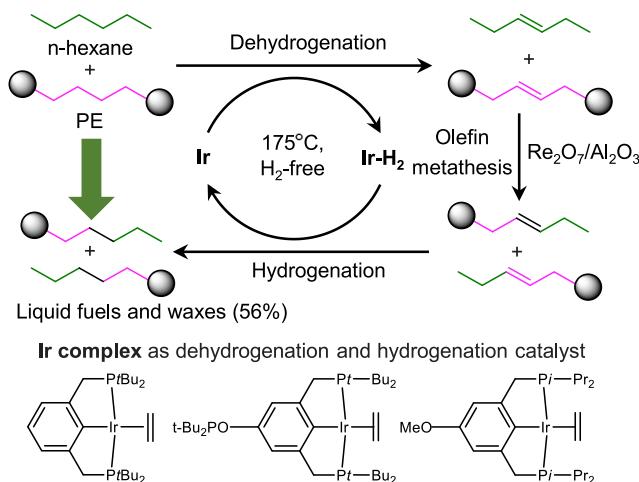


Figure 5. Tandem catalytic cross alkane metathesis of PE

Tandem catalytic cross-alkane metathesis of PE with short alkanes toward liquid fuels and waxes.⁴⁰

generating unsaturated alkenes and Ir-H₂. Next, the Re₂O₇/Al₂O₃ catalyst breaks down the PE chains by scrambling the double bond. Finally, Ir-H₂ hydrogenates the newly formed alkenes to saturated alkanes. PE fragments with long chains can react with the light alkane via multiple CAM processes, eventually leading to short hydrocarbons.

The combination of Pt/WO₃/ZrO₂ and HY zeolites also enables efficient conversion of polyolefins into branched, liquid fuels, including diesel, jet, and gasoline-range hydrocarbons via a tandem catalysis process: polymers are first converted into relatively large olefins or alkanes via hydrocracking over Pt/WO₃/ZrO₂; subsequently, the intermediates diffuse into HY zeolite and then crack to form smaller alkenes.⁹⁵ Because of the synergistic effect of the two catalysts, high yields (85%) of fuel products are obtained under relatively mild temperature (225°C, 3 MPa H₂).

Plastic wastes can also be valorized to more-valuable fuel products, such as jet fuel, with the rapid development of accurate and selective depolymerization and hydrogenolysis technologies. For example, hydrogenolysis of HDPE over a Ru/C catalyst can provide jet-fuel and lubricant-range hydrocarbons with yields as high as 60.8 and 31.6 wt%, respectively.⁹⁶ Theoretically, the chemical composition of plastic wastes is close to that of oxygen-containing liquid fuels, which have distinct advantages over current alkane fuels. Compared with lignocellulosic biomass, the upcycling of plastic wastes to oxygen-containing liquid fuels will consume less, or even zero, external hydrogen if desired reaction pathway can be reached.

UPCYCLING TO MATERIALS

Carbon materials

As abundant and low-cost carbon sources, plastic wastes have been used extensively to produce carbon materials.⁹⁷ The conversion of plastic wastes to versatile carbon materials could not only expand in applications, but could also acquire the benefit of carbon sequestration to some degree. Thanks to the richness and variety of plastic waste and the processing techniques, multifarious carbon materials, including carbon dots (C-dots),⁹⁸ carbon microspheres,⁹⁹ carbon nanofibers,¹⁰⁰ carbon

nanosheets (CNSs),¹⁰¹ three-dimensional (3D) porous carbon,¹⁰² CNTs,^{49,103–105} graphite,¹⁰⁶ and graphene^{107,108} have been manufactured from plastic wastes.

Conversion of plastic wastes to value-added CNTs and graphene, which show tremendous prospects in many domains of science and engineering, represents two important directions of upcycling. Conversion of polyolefin plastics, including PE and PP, to CNTs is usually achieved via two-step process.^{109,110} Polyolefin plastics are first converted to gas products via pyrolysis, and then the gas products are transformed to CNTs over Ni or Fe-based catalysts, with yields limited by the efficiency of both pyrolysis and catalytic CNTs growth process.¹⁰³ Recently, as described in the section of upcycling to fuels, the microwave-initiated catalytic deconstruction over an FeAlO_x catalyst has enabled a one-pot conversion of PE, PP, and PS to MWCNTs without undergoing gas intermediates, providing a simple, rapid, and efficient CNT-production process. A flash Joule heating (FJH) process enables gram-scale, bottom-up synthesis of high-quality flash graphene using mixed plastic waste composed of PET, HDPE, LDPE, PVC, PP, and polyacrylonitrile as the carbon source.¹⁰⁸ This process delivers turbostratic graphene with an interlayer spacing of 3.45 Å, with carbon oligomers, hydrogen, and light hydrocarbons as by-products.¹¹¹ The upcycling of plastic waste to graphene is economically attractive for scale-up because of its low energy consumption (~\$125 in electricity per ton of plastic waste), which is even less than that of producing virgin plastic. Because the FJH process works for various carbon sources, including mixed plastic waste, discarded food, and rubber tires, without the use of a furnace, solvents, or reactive gases, it is a promising method for treating landfill plastic waste.

Plastic-waste-derived carbon materials are promising candidates for adsorbents,¹¹² electrocatalysts,¹¹³ supercapacitors,¹¹⁴ batteries,¹⁰² and solar vapor generation materials.¹¹⁵ For instance, the PE based CNSs are successfully used as transparent conducting film (TCF) to fabricate organic photovoltaic cells.¹⁰¹ The use of PP-derived CNS which has thin thickness (4–4.5 nm) and large specific surface area (3200 m² g⁻¹) with well-defined hierarchical porous structure as symmetric supercapacitor exhibits high energy density.¹¹⁶ The sulfonated carbon scaffold, which is obtained by microwave-promoted sulfonation of LDPE followed by pyrolysis at 900°C, can be employed as interlayer in high-performance lithium-sulfur batteries.¹¹⁷

Polymers

The monomers derived from plastic depolymerization are usually returned to the manufacturer of the original plastic. In addition, the monomers and their derivates made through further chemical or enzymatic transformation can be used for production of new materials. For example, TPA can be converted to 2-pyrone-4,6-dicarboxylic acid, a promising building block for bio-degradable plastic, by two recombinant *Escherichia coli* strains.¹¹⁸ Another option is to incorporate plastic-derived monomers, oligomers, or even polymer fragments into new materials through copolymerization with external building blocks. One-pot upcycling of BPA-PC into high-value poly(aryl ether sulfone)s (PSUs) (Figure 6A), a type of high-performance engineering thermoplastics that can be used for reverse-osmosis and water-purification membranes, medical equipment, and high-temperature applications, has been achieved by depolymerization of BPA-PC into active phenoxides, which are then *in situ* polycondensed with daryl fluorides.¹¹⁹

Aminolysis of PET and BPA-PC provides multifarious modular scaffolds for new polymer production. PET can be transformed to poly(aryl ether sulfone-amide), an advanced thermoplastic material, via aminolysis with 4-aminophenol, followed by

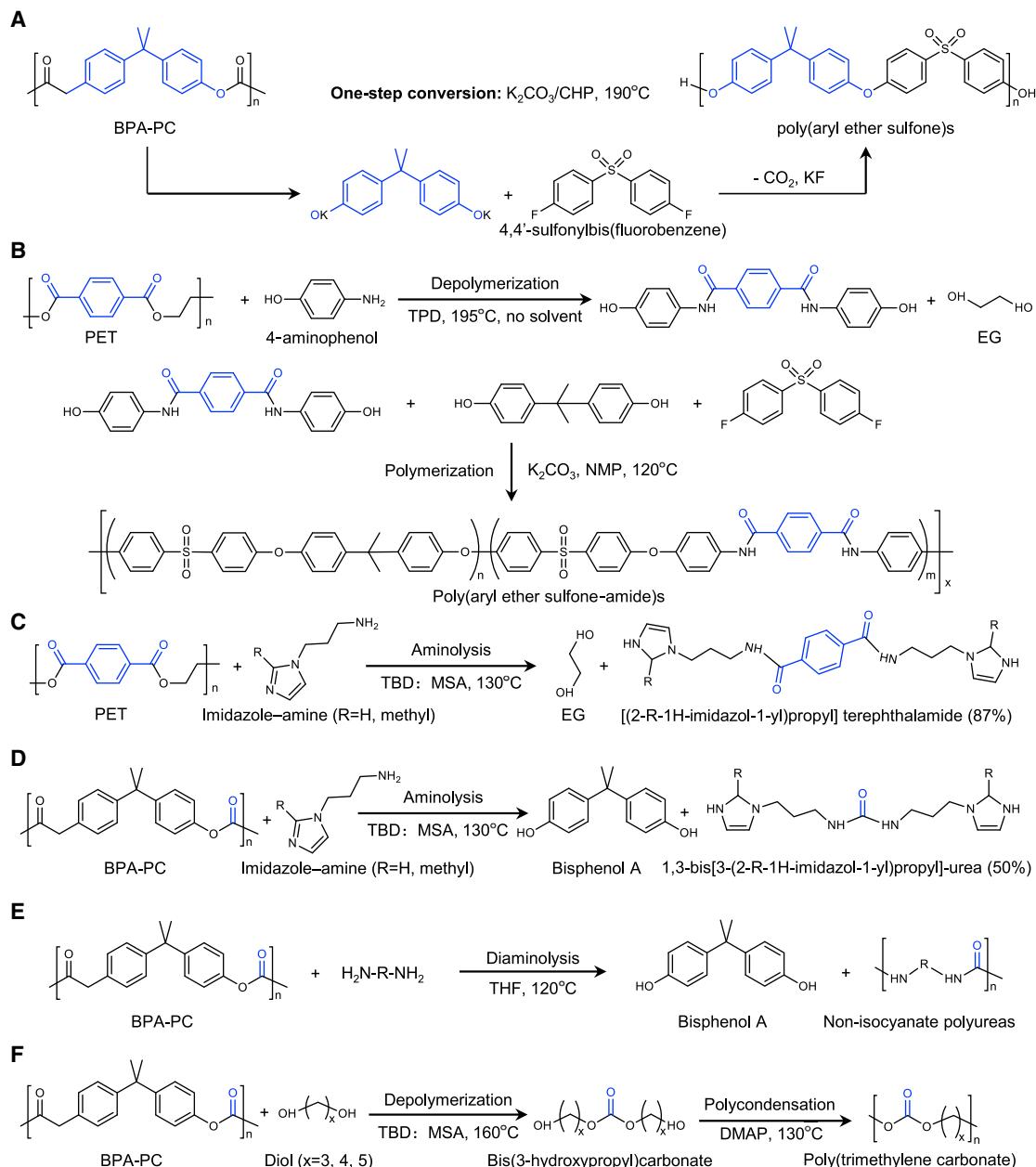


Figure 6. Incorporation of partial monomers into new polymers

(A) One-step conversion of BPA-PC into poly(aryl ether sulfone)s.¹¹⁹

(B) Conversion of PET to poly(aryl ether sulfone-amide).¹²⁰

(C and D) Aminolysis of PET (C) and BPA-PC (D) with imidazole-amines to bis-imidazole monomers.¹²¹

(E) Diaminolysis of BPA-PC wastes with long-chain diamines toward non-isocyanate polyureas.¹²²

(F) Conversion of BPA-PC to aliphatic polycarbonates.¹²³ TBD:MSA, 1,5,7-triazabicyclo[4.4.0]dec-5-ene:methane sulfonic acid; DMAP, *N,N*-dimethyl-4-aminopyridine; CHP, *N*-cyclohexyl-2-pyrrolidone.

nucleophilic aromatic substitution polymerization (Figure 6B).¹²⁰ Aminolysis of PET and BPA-PC with imidazole-amines results in EGs with amide or urea functionality-containing monomers (Figure 6C and Figure 6D), providing an alternative process to produce bis-imidazole monomers without the use of toxic chloride reagents.¹²¹ The PET-derived bis-imidazole monomers can be used to produce high-

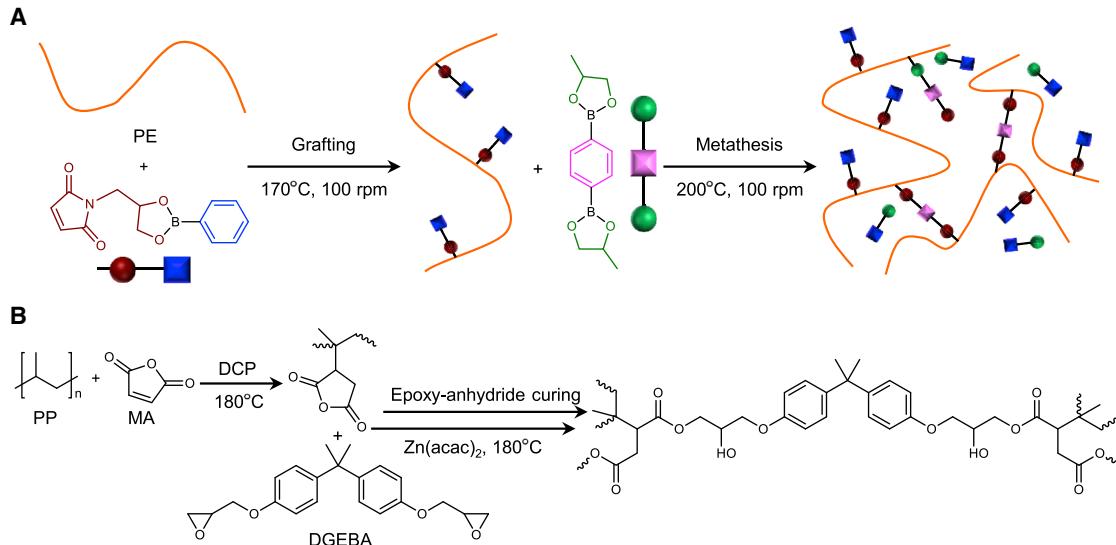


Figure 7. Upcycling of plastic wastes to vitrimers

(A) Conversion of commercial HDPE to vitrimers via metathesis with dioxaborolane.¹³⁰ Adapted with permissions,¹³⁰ copyright 2017, AAAS.
(B) Conversion of PP to vitrimers by grafting MA.¹³¹

molecular-weight ionic polymers, a type of high-performance material with good elastomeric and self-healing property. Similarly, aminolysis of PET with amino-alcohols affords diol terephthalamides, which can be used to synthesize poly(ester-amide)s for new polymer production.¹²⁴ Depolymerization of PET with o-phenylenediamine and 2-aminophenol provides bis-benzimidazole and bis-benzoxazole, respectively, which are promising feedstocks for medicines, high-performance polymers, and organic electronics.¹²⁵ The diaminolysis of BPA-PC with long-chain diamines in THF produces bisphenol A and non-isocyanate polyureas (Figure 6E) through a non-isocyanate and one-pot route.¹²² The depolymerization of BPA-PC with aliphatic diols produces bisphenol A and the corresponding carbonate-containing diols (Figure 6F), which can be polymerized into a series of value-added aliphatic polycarbonates with ionic conductivity as potential polymer electrolytes for solid-state batteries.¹²³

The development of covalent adaptable networks that can transit their behavior under specific stimuli has long been of interest to researchers as a promising approach toward bridging the gap between thermoplastics and thermosets.^{126,127} Upcycling of post-consumer, plastic waste into covalent adaptable networks could impart recyclability and retain many of the beneficial properties of the thermoset materials. Vitrimers are one typical type of a covalent, adaptable network that combines the advantages of thermoplastics (light, tough, and easy to process, assemble, and recycle through heating) and thermosets (high mechanical, thermal, and chemical resistance).^{126,128,129} Because vitrimers are composed of polymer networks that undergo rearrangement of chemical bonds and topology via, for example, exchange reactions, without reducing the number of chemical bonds and cross-links, they can reversibly switch between thermosets and thermoplastics.¹³⁰ Commercial HDPE, a typical thermoplastic, has been converted to high-performance vitrimers through grafting of maleimides bearing dioxaborolane functionalities onto HDPE, followed by cross-linking of functional polymers containing pendant dioxaborolane units, via metathesis with a bis-dioxaborolane (Figure 7A).¹³⁰ Compared with the original HDPE, the resulting vitrimers exhibit markedly improved melt strength,

dimensional stability at elevated temperatures, and solvent and environmental stress-cracking resistance. Moreover, these vitrimers can be extruded or injection-molded, akin to thermoplastics, which is a prominent advantage over thermosets and vitrimers produced by traditional cross-linking methods. The dioxaborolane metathesis method also enables the direct processing of incompatible polymers, providing a promising approach for the valorization of plastic waste without sorting. Analogously, conversion of polyolefins, including PP and PE, to high-performance vitrimers (Figure 7B) has been achieved by grafting maleic anhydride (MA) using di-cumyl peroxide (DCP) as a free-radical initiator, followed by epoxy-anhydride curing with a di-functional epoxy (DGEBA).¹³¹ Introducing dibutyltin dilaurate could impart malleability into commercial cross-linked PUR, a typical thermoset material, thus enabling its reprocessing at high temperatures via dynamic carbamate-exchange reaction.¹³² After further twin-screw extrusion, the PUR filaments or films obtained show elastomeric or rigid thermoset mechanical properties. Functionalization of polyisoprene and PS by azidoformate grafting agents though reactive processing affords vitrimers with good creep resistance at room temperature and good mechanical properties.¹³³ Incorporating dioxaborolane during the polymerization of methyl methacrylate¹³⁰ or treating vinyl-monomer-derived prepolymers with a trifunctional amine¹³⁴ could produce PMMA vitrimers, but direct upcycling of post-consumer PMMA into vitrimers has not, to our knowledge, been achieved.

Post-functionalization is a potential strategy to impart certain functionalities and unique properties to plastics and to preserve the integrity of the polymer skeleton.^{135,136} For instance, TBD-catalyzed or metal-catalyzed transesterification of acrylic polymers, such as poly(methyl acrylate) (PMA) and PMMA in the presence of alcohol and amine nucleophiles, combined with reversible-addition fragmentation chain transfer, allows for the precise functionalization of sterically differentiated acrylic copolymers and polymeric chain ends, providing a new route for upcycling of adhesive and coating waste into value-added materials.^{137,138} In contrast, controlled defunctionalization may also afford unexpected materials. For example, PMA can be converted to PP via $B(C_6F_5)_3$ -catalyzed deoxygenation in the presence of silane.¹³⁹ In addition, grafting of acrylic acid, poly(propylene imine) dendrimer,¹⁰⁰ and acrylonitrile¹⁴⁰ onto PP could produce functionalized adsorbents.

The integration of plastic valorization with biomass resources has provided an effective strategy to dramatically improve economic and environmental benefits. As a proof-of-concept, the combination of partially glycolized PET with bio-based monomers enables the upcycling of PET waste into high-value composite materials (Figure 8A), synchronously incentivizing plastic reclamation and the actual application of biomass-derived chemicals.³⁹ PET is partially glycolized with a diol (EG or 1,4-butanediol) over a titanium-butoxide catalyst. Afterward, glycolized PET is converted to unsaturated polyesters (UPEs). Fiberglass-reinforced plastics (FRPs) are produced by dissolving the UPEs in a reactive diluent in the presence of a free-radical initiator. Alternatively, FRPs can also be directly synthesized from partially deconstructed PET with olefinic carboxylic acid via polymerization followed by cross-coupling by free-radical initiator. Compared with petroleum-based FRPs, the two types of FRPs prepared from PET show substantially improved material properties with a total supply-chain energy savings of 57% and GHG emission reduction of 40%. Moreover, PET-derived FRPs have a higher selling price (\$1.85 USD/lb) than PET resin does (\$0.81 USD/lb) with 75% lower energy consumption than that of returning the product to bottle-grade PET resin. Similarly, transesterification of poly(glycolic acid) (PGA with biodegraded γ -butyrolactone [BL] as both the comonomer and the solvent yields a sequence-defined copolymer

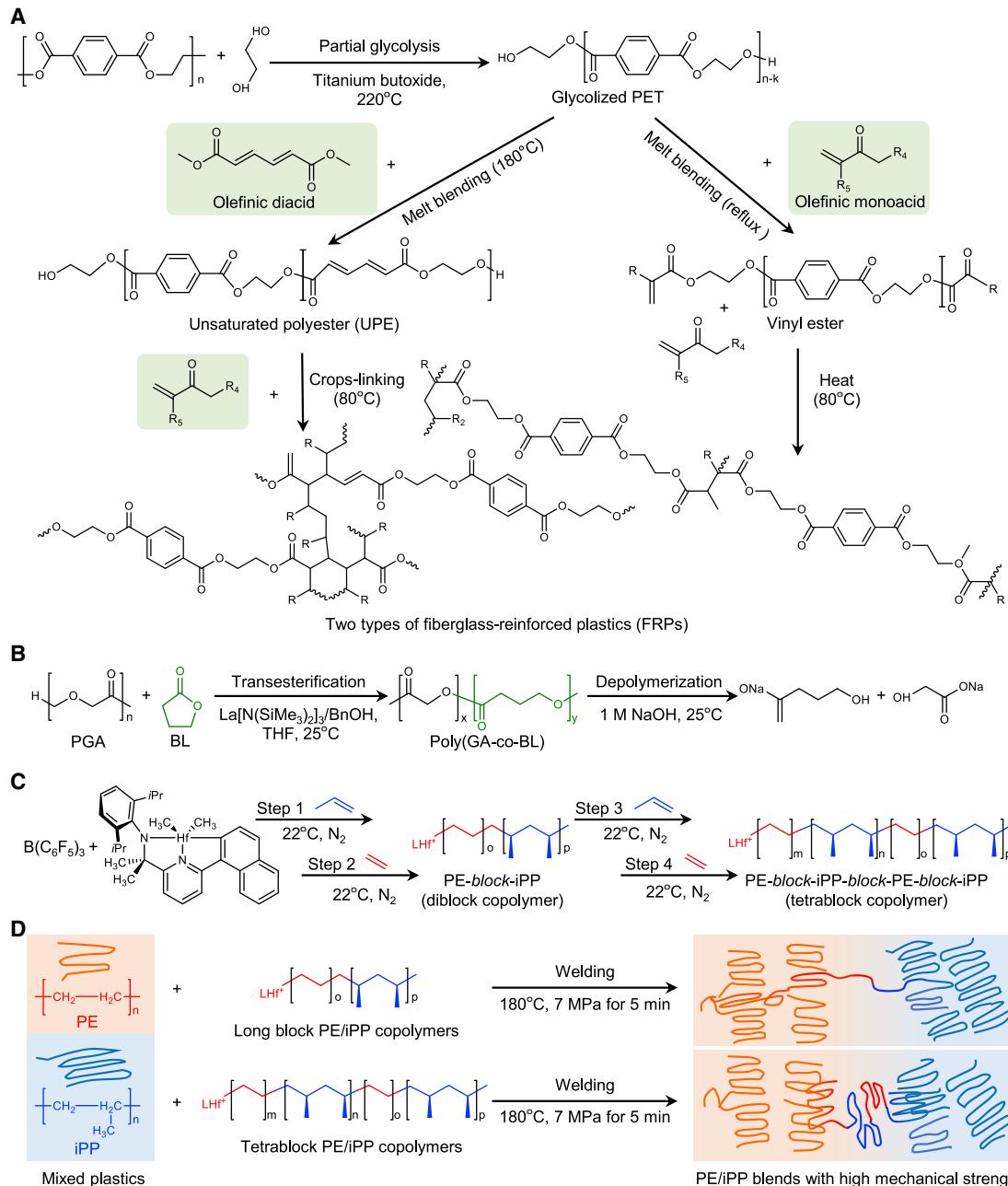


Figure 8. Incorporation of plastic fragments into new materials

(A) Upcycling of PET to FRPs via partial glycolysis, followed by combination with biomass-derived monomers.³⁹

(B) Transesterification of PGA with γ -butyrolactone into a copolymer.¹⁴¹

(C and D) Controlled isoselective polymerization of propylene and ethylene toward multiblock copolymers over isoselective pyridylamidohafnium catalyst (iPr, isopropyl) activated by $\text{B}(\text{C}_6\text{F}_5)_3$ (C) and the use of copolymers to compatibilize commercial PE and iPP (D).¹⁴² (D) was adapted with permissions,¹⁴² copyright 2017, AAAS.

poly(GA-co-BL)) (Figure 8B), which is not only chemically recyclable but also exhibits improved thermal stability ($\geq 44^\circ\text{C}$) than PGA.¹⁴¹

The use of plastic waste as the feedstock in additive manufacturing (AM) maps out a new path for plastic recycling and upcycling toward a circular economy.¹⁴³ For instance,

blends of HDPE waste with low-molecular-weight PP and MA-modified PP in a specified formula can be converted into filaments for 3D printing with properties comparable to PLA, one of the most widely used thermoplastics for AM.¹⁴⁴ In another example, the waste from children's toys, which are composed of acrylonitrile butadiene styrene, were successfully converted to filaments comparable to virgin materials.¹⁴⁵

Composite materials

Current plastic-recycling technologies require stringent sorting and separation steps to recover pure polymer as the feedstock because different types of polymers in the actual plastic waste are usually immiscible.^{27,146} Because of the formation of separate phases with weak mechanical strength at the interfaces, the melted blends are brittle, even when just containing a small quantity of the other type of polymer.¹⁴⁷ The use of compatibilizers as molecular stitches to anchor different polymers allows for direct upcycling of mixed plastic waste toward high-value materials, exempting the costly and time-intensive sorting step.^{27,147–149} For example, a series of semicrystalline PE/iPP multiblock copolymers, which can be prepared by controlled isoselective polymerization of propylene and ethylene (Figure 8C), exhibited superior efficiency for the compatibilization of PE and iPP.¹⁴² PE-block-iPP diblock copolymers (Figure 8D) can weld common grades of commercial PE and iPP together only when the molecular weight of the blocks exceeds a threshold. In contrast, just 1% of tetrablock copolymer could transform mixed polyolefin municipal waste (typically PE:iPP = 70:30) into mechanically tough blends with considerably higher strain at the break point ($\epsilon_b = 450\%$) than that of direct blending ($\epsilon_b = 12\%$) because of the formation of entangled loops, which can stitch the homopolymers together effectively and form block copolymer films upon crystallization. Analogously, the multiblock copolymers consisting of PP and polar PU segments can be used as a versatile compatibilizer for PP and polar polymers, including poly(methyl methacrylate), PVC, and poly(vinylidene difluoride).¹⁵⁰ Poly(ethylene terephthalate)-polyethylene multiblock copolymers also serve as both the adhesive-promoting layer and the compatibilizer to recycle PET/PE mixed waste.¹⁵¹ With MA, a commercial compatibilizer, recycled PP and PET blends can be remolded to water pipes with improved flexural properties than that of virgin PP without compromising its impact properties.¹⁵² In addition, block copolymers prepared by controlled polymerization could be used to prepare vitrimers with considerably better resistance to macroscopic deformation than their analogs derived from statistical copolymers.¹⁵³ Therefore, in the future, it may be possible to convert plastic waste to high-performance vitrimers via block copolymers as intermediates.

In addition to the blending of different types of polymers, plastic waste can also be recombined with other types of materials toward the manufacture of composite and hybrid materials. The use of plastic waste to displace virgin plastic offers an effective way to reduce the cost of fabricating commercial composite materials. For example, PET/cotton blend fabrics are widely used in garments and home textiles, accounting for more than 50% of textiles.¹⁵⁴ Polyester waste can be used as the feedstock to produce cotton-based composite fabric with improved mechanical properties.¹⁵⁵ Polyester/cotton blend fabrics can be further converted to a fiber-reinforced composite through co-depositing of polyethylenimine and catechol to enhance the interfacial bonding of the fiber matrix.¹⁵⁴ Pseudopolyrotaxane inclusion complex with improved thermal stability and optical properties can be prepared from styrofoam (also called expanded polystyrene), by sulphonation, followed by encapsulation of γ -cyclodextrin.¹⁵⁶ Both PET and PLA can be used as inker sources to synthesize value-added metal-organic frameworks (MOFs) through either one-pot or two-step processes, using the corresponding monomers as linkers.^{157,158} The use of PET waste

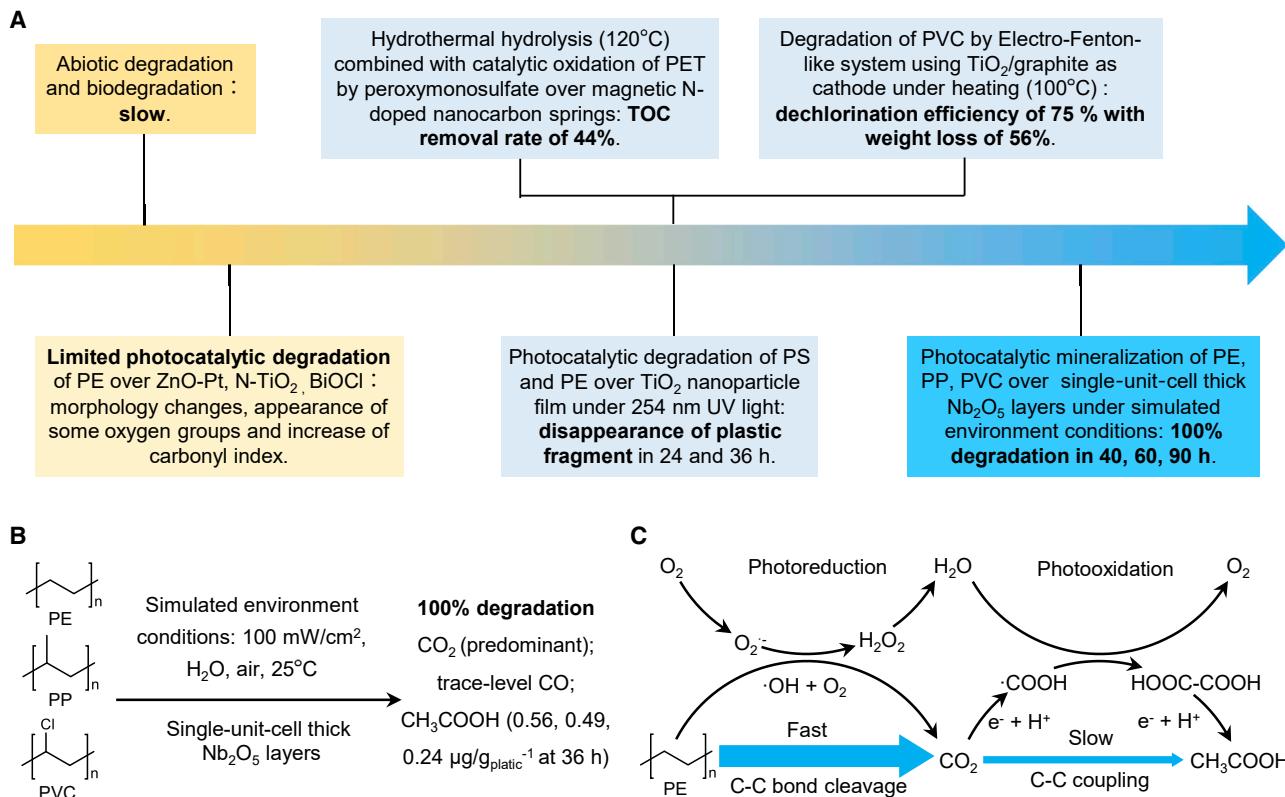


Figure 9. Research highlights in catalytic degradation of plastic wastes

(A) Trend of the development of catalytic degradation technologies.

(B and C) Degradation of PE, PP, and PVC under simulated natural environment conditions using single-unit-cell-thick Nb₂O₅ layers as photocatalyst (B) and the proposed reaction mechanism (C).⁶⁵

as the source and support to grow UiO-66 MOF provides hybrid PET@UiO-66 material.¹⁵⁹ As a novel sorbent, PET@UiO-66 exhibits obvious advantages, such as high adsorption capacity and rate, stability and recyclability and 100 times enhanced permeability than UiO-66 powder.

CATALYTIC DEGRADATION

Advanced oxidation processes (AOPs), including Fenton reactions, Fenton-like reactions, and photocatalytic oxidation have offered a potential portfolio for the catalytic degradation of plastic waste (Figure 9A). These technologies were primarily designed and developed for the degradation of soluble organic pollutants with low molecular weights. Previously, AOPs have been widely investigated to degrade bisphenols and phthalates plasticizers, such as bisphenol A and diethyl phthalate.¹⁶⁰ A few hydrolyzable plastics can be depolymerized to monomers and then be further treated in the form of molecules by AOPs. For instance, the degradation of polyesters can be achieved by depolymerizing ester bonds by 80% hydrazine hydrate along with NaOH, followed by the Fenton reaction.¹⁶¹ Nevertheless, most plastics are insoluble macromolecules, which cannot be depolymerized under normal conditions. To achieve efficient degradation of plastic waste, AOPs must be improved or combined with other means, according to their structural features.

AOPs and hydrothermal hydrolysis have been successfully integrated to degrade PE-based microplastics into environmentally benign organic intermediates in

water.⁶⁴ The magnetic N-doped nanocarbon springs (Mn@NCNTs) catalyst, which is prepared by encapsulating manganese carbide nanoparticles into helically N-doped carbon nanotubes, provides excellent performance for the degradation of microplastics (size ranges from 0.01 to 1.5 mm) from commercial facial cleanser by activating peroxyomonosulfate to generate sulfate radicals and hydroxyl radicals ($\cdot\text{OH}$). Microplastic removal efficiency (weight loss) of 44% was achieved at 120°C for 8 h. The degradation products are mainly composed of low-molecular-weight and less-toxic organic compounds, which can be used as a carbon source for algae cultivation. The removal efficiency declines by 45% in the fifth consecutive cycle.

Electro-Fenton-like systems could promote the degradation of PVC microplastics via the cooperation of reduction and oxidation reactions. Using TiO₂/graphite as the cathode, the potentiostatic electrolysis at -0.7 V versus Ag/AgCl under heat (100°C) for 6 h attains a dechlorination efficiency of 75% with a PVC weight loss of 56%.¹⁶² The dechlorination of PVC is achieved through direct reduction by the applied cathode potential, whereas the cleavage of the PVC backbone is dominated by $\cdot\text{OH}$.

In addition to Fenton and Fenton-like reactions, photocatalytic oxidation have been studied extensively for catalytic degradation of plastic waste. Under visible light, degradation of PE microplastics (1 mm × 1 mm) over a plasmonic platinum/zinc oxide nanorod (ZnO-Pt) catalyst¹⁶³ and degradation of LDPE-bag debris (in the form of films with sizes from 3 mm × 3 mm to 5 mm × 5 mm) over a mesoporous N-TiO₂ catalyst¹⁶⁴ in an aqueous solution only leads to a slight deconstruction of plastic, including morphology changes, the appearance of some oxygen groups, and an increase of carbonyl index, without reporting weight loss. The degradation of HDPE microspheres (200–250 μm) in an aqueous solution over a hydroxy-rich, ultrathin BiOCl catalyst under simulated solar light for 5 h attains a weight loss of 5.38%.¹⁶⁵ Comparatively, the degradation of smaller plastic fragments is much easier than the larger ones.^{164,165} Recently, efficient degradation of small-size PS microspheres (5 μm) and PE (approximately 50 × 50 μm) to CO₂ via solid-phase photodegradation was achieved over a TiO₂ nanoparticle film prepared with Triton X-100,¹⁵ but the degradation efficiency was evaluated by the reduction in volume of the PS sphere, which was estimated by scanning electron microscopy (SEM) analysis, instead of the more-precise weight analysis. Complete disappearance of PS and PE in SEM images was achieved under 254 nm ultraviolet (UV) light within 24 and 36 h, respectively. The degradation efficiency of microplastic at the solid-solid interface (microplastic-TiO₂) is considerably higher than that in the liquid phase because the reactive species can attack the polymers directly without any hindrance through the direct contact of microplastic with the TiO₂ film.

Complete mineralization of PE, PP, and PVC into CO₂ (Figure 9B) has been achieved via photocatalytic degradation using single-unit-cell-thick Nb₂O₅ layers as photocatalyst under simulated natural environment conditions (Xe lamp with a standard AM 1.5G filter, 100 mW/cm², H₂O, air, room temperature) within 40, 60, and 90 h, respectively.⁶⁵ The 100% mineralization was demonstrated by the vanished characteristic peaks of the plastics in X-ray diffraction (XRD) and Raman spectra, as well as by the formation of CO₂ with total moles close to the C content in the feedstock. The 100% mineralization under simulated environment conditions is inspiring—which has not been reached by other AOPs. Because the valence band (+2.5 V versus normal the hydrogen electrode [NHE; pH 7]) of Nb₂O₅ is higher than the redox potential of H₂O/ $\cdot\text{OH}$ (+2.32 V NHE) and the conduction band (0.9 V versus NHE) is lower than the required potentials of CO₂ reduction (0.6 V versus NHE, pH = 7),

the Nb_2O_5 catalyst allows a one-pot conversion of the plastics to acetic acid (CH_3COOH) through a sequential, photoinduced C–C bond cleavage and coupling pathway. Along with the photodegradation of the plastic toward CO_2 through oxidative C–C cleavage triggered by O_2 and $\cdot\text{OH}$ radicals (Figure 9C), the generated CO_2 is further selectively photoreduced by H^+ and e^- toward CH_3COOH , a potential high-energy-density C_2 fuels. Because of the low rate of photoreduction, the CH_3COOH yields after 36 h were just 0.56, 0.49, and $0.24 \mu\text{g/g}_{\text{plastic}}^{-1}$ for PE, PP, and PVC, respectively. Similarly, vanadium photocatalysts have been reported to be capable of catalyzing the cascade carbon–carbon-bond scission of a series of hydroxyl-terminated polymers, including polyethylene glycol and polyethylene mono-alcohol (a model of PE) under visible light irradiation without alkaline pretreatment, but their catalytic performance for actual plastic waste was not provided.¹⁶⁶

Although noteworthy progress have been achieved, the application of AOPs to remediate microplastic pollution in actual wastewater and natural aquatic environments faces considerable challenges. Except for the Nb_2O_5 -based photocatalytic system, the degradation of microplastics in most catalytic systems is very slow at ambient temperature, whereas heating actual wastewater and natural aquatic environments to the evaluated temperatures requires a large quantity of energy. The coexistence of microplastics with biodegradable organic matter may consume large amounts of oxidizing agents, increasing the cost considerably. Furthermore, the reuse of catalysts seems to be impossible because of the difficulties in catalyst recovery. Therefore, much effort is required to develop more-powerful and selective degradation technologies.

CONCLUSIONS AND FUTURE PROSPECTS

Although there is no panacea for the complicated and successional evolutive plastics problem, upcycling and catalytic degradation map out two important routes toward the vision of a sustainable and zero-pollution future. The concept of upcycling was developed to ameliorate the intrinsic drawbacks of traditional recycling technologies and to improve the overall benefits through unearthing of products of high value. The ready availability and diversity of plastic waste represent a largely under-developed opportunity. Tailored upcycling processes for each type of plastic are the most likely approach to deliver maximal economic and environmental benefits.^{31,57} Compared with conventional recycling processes and many industrialized processes based on fossil resources, some upcycling processes and products have already been shown to have distinct advantages in both high-value areas and basic applications. Ascertaining the embedded value in plastic waste, which is present in the form of carbon, hydrogen, chemicals, energy, and macromolecular structures, might not only reduce the generation of undesired side-products and the consumption of energy and other external resources but also contribute to the improvement of conversion efficiency, eventually elevating the overall benefits. Furthermore, some upcycling processes have shown superiority in the handling of real-world, mixed, or contaminated plastic waste with a decrease in process complexity and cost. Importantly, most upcycling processes are compatible with both existing sorting and recycling processes, and the feasibility of using or retrofitting existing infrastructure might facilitate an uptake in new routes. The lucrative upcycling processes would not only enhance the reclaiming rate but also, in turn, expedite the development and actual application of traditional recycling processes. Indeed, there are also some controversial upcycling processes that involve the use of toxic reagents or result in additional issues, such as secondary pollution. Notably, the resulting materials do not necessarily mean they can be subjected to a continuous recycling and upcycling process.

Conferring degradability or recyclability into the target materials during the upcycling process is significant toward establishing an ideal, sustainable, closed loop.

Upcycling technologies can be enhanced by the following endeavors. Advanced catalytic methods must be established to improve reaction efficiency. Generally, both upcycling and recycling processes are restrained by limited solid-solid contact efficiency between the recalcitrant plastic substrate and heterogenous catalysts, intricate reaction networks, and undesired degradation of the target products. Hence, the development of quantum dot catalysts, homogeneous catalysts, enzyme-mimetic catalysts, tandem catalysis strategies, stabilization chemistry, and the coupling of different catalytic technologies is a potential option for solving these bottlenecks. In addition, the catalysts should have a high tolerance for air, moisture, and organic or metal salt contaminants.³⁷ Beyond catalysts, the screening of applicable solvents able to swell, dissolve, or selectively separate different polymers¹⁶⁷ or able to remove colorants and other additives is also essential.³¹ A comprehensive upcycling roadmap should be established and then be combined with recycling processes on the cusp of commercialization to make them available for most plastic waste streams. It should be emphasized that, under the framework of upcycling, plastic waste can be considered an important and unique resource that ranges between fossil and biomass resources, not solely a troubling litter. Therefore, the development of plastic upcycling should learn from the well-established oil refining processes and rapidly growing biorefinery processes. The drop-in integration of plastic upcycling with oil refining, biorefinery, and CO₂ use processes would foster new reaction routes and products. In fact, similar chemical-bond activation strategies,^{168,169} enzymatic decomposition mechanisms,²⁹ and photoreforming process⁸⁶ have already been successfully applied for the conversion of both biomass and plastic waste. In addition, one-size-fit-all upcycling approaches for mixed plastic waste should be explored to obviate the need for sorting, separating, and purifying.²⁷ Whether upcycling processes are sustainable and technically, economically, and environmentally viable depends on the entire life cycle from collection and sorting of plastic waste to production of high-value products to end-of-life management. Therefore, the economic benefits and environmental impacts must be evaluated on a case-by-case basis with rigid criteria and be compared with appropriate benchmarks before their commercialization.

The development of degradation technologies is still at its early stages. Up until now, most degradation methods developed for molecular pollutants have been substantiated to be ineffective, whereas a few of catalytic processes have already showed the possibility of degrading plastic waste under artificially optimized harsh conditions with a series of ancillary measures and superiority over biological degradation. More scientific proof, based on tracing experiments or monitoring of degradation products using mass balances, is required to confirm the claimed degradation and mineralization.³³ Achieving efficient degradation of real-world plastic waste under actual environmental conditions remains an important and challenging task for future research. The aforementioned strategies aimed at improving the upcycling processes should be helpful for enhancing catalytic degradation technologies; among which, the selective contact and binding of substrates with catalysts or the screening of cheap and environmentally friendly catalysts and oxidants is of great importance. Compared with mineralization, partial and selective degradation toward environmentally benign products or degradable products, followed by spontaneous biodegradation seems to be a more-viable option for reducing the consumption of energy and oxidants.

The ongoing modification of currently used plastic materials and the burgeoning invention of new polymers create both opportunities and challenges for plastic

recycling, upcycling, and degradation. Meanwhile, the use-pattern and scale of plastic materials are also varying rapidly.¹⁷⁰ Many plastic packaging materials manufactured in modern industry are multilayer plastic films composed of distinct polymer layers.^{8,167} The complex composition and tough structure considerably increase the difficulty of sorting and reprocessing, impeding the economic benefits of recycling and upcycling. The design of recyclable plastics that undergo reversible (de)polymerization^{171,172} and recyclable thermosetting plastics containing dynamic covalent bonds^{173–175} would not only promote chemical and mechanical recycling but also influence upcycling processes. In addition, the possible contamination of plastic wastes by the decomposition of degradable plastics may also increase the separation costs and reduce the performance of recovered materials.³⁵

Another pivotal environmental concern associated with plastics is the exhaustion of non-renewable fossil resources. The most hopeful solution to this problem is to develop more “sustainable” polymers from CO₂ and renewable resources, in particular, plant-based feedstocks, such as cellulose, lignin, other polysaccharides, deoxyribonucleic acid, polyhydroxyalkanoates, sugars, vegetable oils, and terpenes; however, most current routes toward renewable feedstocks are far from cost effective relative to conventional routes.^{2,34,176–183} Furthermore, sustainable polymers from renewable resources do not mean they are also degradable or recyclable. Although several recyclable and degradable polymers from renewable sources have been successfully designed in the laboratory,^{178,184–188} the ideal integration of sustainability, degradability (or recyclability), usability, and low-cost, in practice, is still a huge challenge. Therefore, sustainable polymers also require the corresponding recycling, upcycling, and degradation technologies once they are produced on a large scale.

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AUTHOR CONTRIBUTIONS

Q.H. proposed the topic of the review and wrote the manuscript. M.Z., H.Q., Y.N., X.B., T.X., M.L., and Q.L. investigated the literature. M.J. revised a draft of the review.

DECLARATION OF INTERESTS

There are no conflicts of interest to declare.

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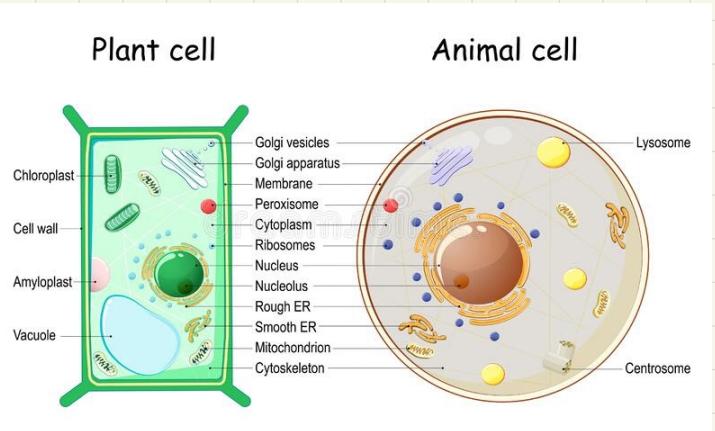
What is an organell?

→ organs of the cell that keep us alive.

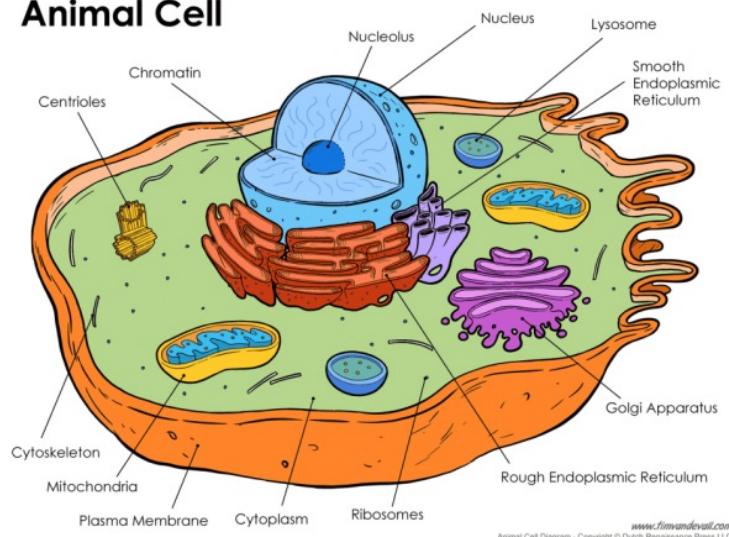
ANIMAL CELL:

main components of the cell

- 1) Plasma membrane - Lipid bilayer
- membrane protein
- 2) Cytoplasm - mostly water, soup of our cell
- 3) Nuclei - contains DNA
- ribosomes



Animal Cell



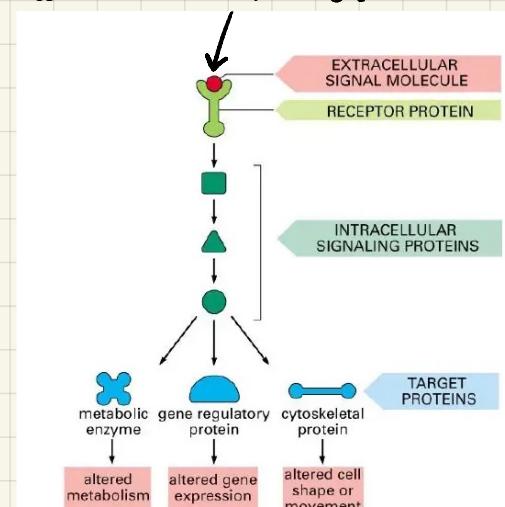
PLANT CELL: same components as animal cell but with extra:

- cytoplasm
- cell wall
- vacuole

Cybernetics: the science that studies the homeostasis of life
↓
maintaining balance & fluctuation

in order to maintain this balance, first we need to sense the environment

- 1) Change metabolism
- 2) Change cytoskeleton
- 3) altered gene expression



Information processing

iGEM - International Genetically Engineered Machine

- 1) Present the problem
- 2) Present possible solutions

→ make diagrams

In 2020, a major advance saw scientists identifying another enzyme that could degrade PET in just 10 hours¹⁰. The research screened a large variety of bacteria and enzymes for potential candidates, including the leaf-branch compost cutinase, LCC, that was first discovered in 2012. Hundreds of mutant PET hydrolase enzymes were then produced by varying amino acids at the binding site and improving thermal stability. Bacterial mutants were then screened to identify efficient PET decomposers. After running this process for multiple rounds, a mutant enzyme was isolated that is 10,000 times more efficient in degrading PET than the native LCC. It is also stable at 72°C, close to the melting temperature of PET. This finding contributes significantly towards attaining the infinite recycling of PET and is already at a pilot industrial stage¹⁰.

PET biodegradation has been extensively studied because esterase enzymes (enzymes that split esters into an acid and an alcohol) are abundant in nature². Reports on the biological degradation of PET or its utilization to support microbial growth are, however, infrequent. Some organisms from the filamentous fungi group, *Fusarium oxysporum* and *Fusarium solani*, have been grown on a mineral medium containing PET yarns³.

In 2016, Yoshida et al⁴ reported the discovery and characterization of the soil bacterium strain, *Ideonella sakaiensis* 201-F6, found growing in PET-contaminated sediment near a plastic recycling facility in Japan. This gram-negative, aerobic, rod-shaped bacterium has the remarkable ability to use PET as its major carbon and energy source for growth.

I.sakaiensis employs a two-enzyme system to depolymerize PET to its building blocks, TPA and EG, which are further catabolized to a carbon and energy source. One of the two enzymes, ISF6_4831 protein, hydrolyzes and breaks ester linkages. With a preference for aromatic rather than aliphatic esters, and a specific inclination towards PET, it is designated as a PET hydrolase (PETase). The PETase enzyme in *I. sakaiensis* is a cutinase-like serine hydrolase that attacks the PET polymer, releasing bis(2-hydroxyethyl) terephthalate (BHET), mono(2-hydroxyethyl) terephthalate (MHET) and TPA. PETase further cleaves BHET to MHET and EG. The second enzyme, ISF6_0224 protein, MHET hydrolase (MHETase), further hydrolyzes the soluble MHET to produce TPA and EG (Fig. 2). Both enzymes are required, likely synergistically, to enzymatically convert PET into its two environmentally benign monomers, TPA and EG4, making it possible to fully recycle PET.

CHEWING GUM

made out of plastic
→ polyethylene gum base
how to do «depolymerisation»

interesting enzyme: LCC

problem = unstable at high temp.

To achieve depolymerization, scientists have looked to nature, searching for microbial enzymes that can break down plastics. In 2012, researchers at Osaka University discovered an enzyme in a compost heap that can break down one of the world's most used plastics: **polyethylene terephthalate (PET, CAS Registry Number 25038-59-9, formula $(C_{10}H_8O_4)_n$)**.

The enzyme, known as **leaf-branch compost cutinase (LCC)**, breaks the bonds between PET monomers, but it is intolerant to the 65°C softening temperature of PET, denaturing after a few days of working at this temperature and limiting its industrial practicability. Since depolymerization can only take place in molten plastic, enzymes must be stable at increased temperatures

Source = CAS

American
Chemical
Society

AGRI ZERO

from forage to farm & back

worlds - 1, 2, 3, 4

first world: "developed" capitalist economies - USA, Western Europe

second world: socialist economies - USSR back in Cold War

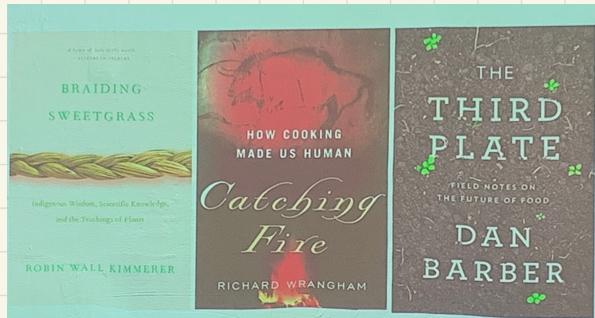
third world: "the global south"
resource procuring nations

fourth world: migratory & transitory countries

"Hunter-Gatherer" - the term hunting refers to Nomadic herding

ITK - Indigenous Technical Knowledge

Tacit knowledge - tactile, hand knowledge



Books on agricultural knowledge
which led to the development of humans

Becoming sedentary - deciding to stay in fertile areas, 12,000 years ago

Due to floods from end of ice age)

new species of wheat - Emmer wheat
↳ easy to peel, easy to grow in fertile area

= beginning of urbanism to protect wheat & preserve this from of wealth

MESOPOTAMIA

Domestication: who domesticated who?

WW2 - synthesize nitrate & nitrite → make bombs

BUT ALSO fertiliser

The Importance of context

Permaculture + Agroecology

→ the edge: holds the most interesting species because they have to interact with one another

Self-sufficiency in Valdaura -

technology choice / Small is beautiful

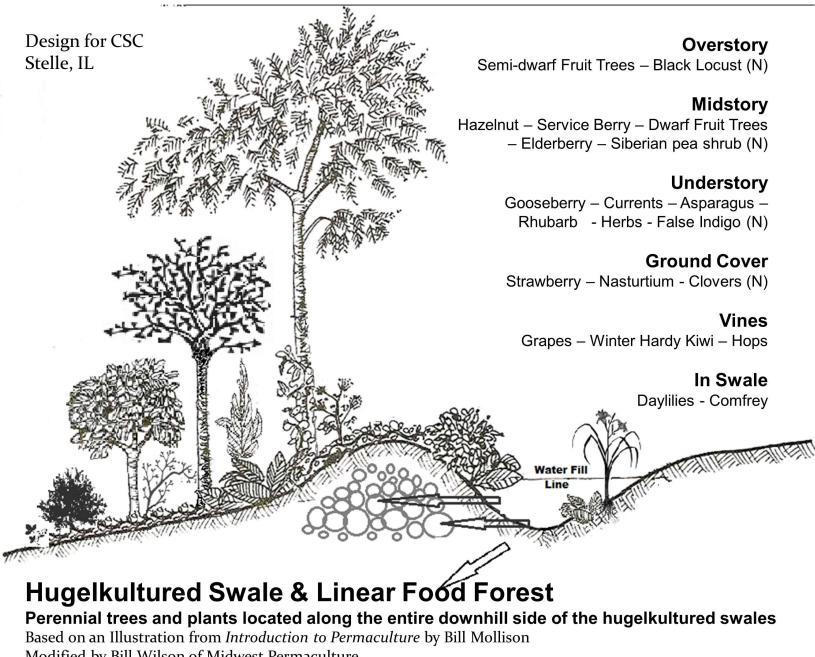
Data as a lens

Project: Romi - EU funded

Robotics for Microfarming

Poly cultures: Many different crops - biodiversity

open soil = waste of light → healthy farms = can't see soil



synergy between agriculture & computing: do things with least amount of effort

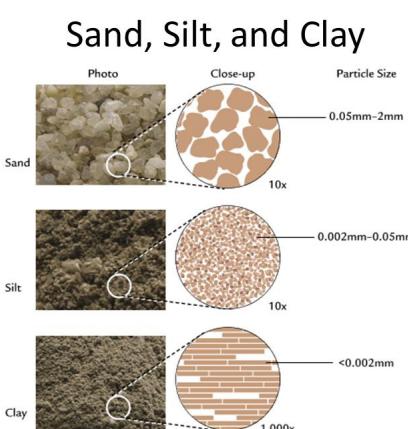
Computational Agro-ecology will be a tool to engage young generations in agriculture → these generations are no longer interested

SOIL - a living biome because it

cycles of composition & decomposition

Geophysical loam mineral

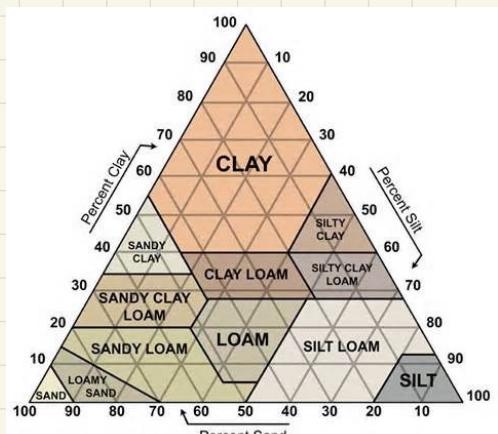
Meta genomic analysis - reading DNA code, sequence & compare results
↓
meta because large scale,
not single organism / being
= looks at everything at the same time



different types of particle sizes

bigger particles = absorb more water

smaller particles = easier to break down



Soil Texture & Associated Permeability		
SAND	SANDY LOAM	CLAY
RAPID	MODERATE	VERY SLOW

fluffy soil to grow plants

LOAM = organic part of soil
↳ compost?

humus = ready-made top soil → the best to put on top & grow plants



} different horizons
→ we are interested in A horizon (top layer)

Open source problems - how to brand & earn money

Monsanto herbicides

No Nicotine

5 TENETS OF AGRICULTURE
↳ 5 pillars

optimise the waste & production in Agriculture to make it regenerative & sustainable

CONVENTIONAL AGRICULTURE → how to transition?
what technologies / practices?

Ploidy

HAPLOID → 1 set of eggs / sperm

DIPLOID → 2 sets = human

Chromosomes - some organisms have more than we do
= evolutionary complexity

↓
grass & plants have more ecological adaptation
than we do → adaptable

+ BIO MATERIALS +

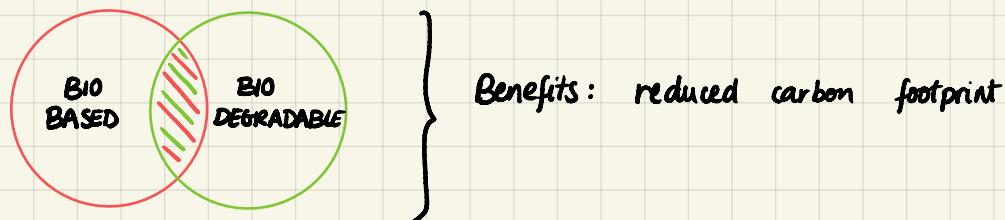
plastic = malleable, moldable

precious plastics - remolding petrol-based plastics

↳ lose quality & malleability every time they're re-used

bioplastics = could be biodegradable or not

→ bio-based just means part of it contains bio-material



Benefits: reduced carbon footprint

what about ocean-degradable plastic?

↳ dissolve in saline solution

what about farm waste-based materials?

↳ from pruning, weeding, cutting

STOICHIOMETRY

