

POTENTIAL CONTRIBUTION OF NANOTECHNOLOGY TO THE CIRCULAR ECONOMY OF PLASTIC MATERIALS

Monica Distaso*

Institute of Particle Technology, Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU)
Cauerstraße 4, D-91058 Erlangen

Interdisciplinary Center for Functional Particle Systems, Friedrich-Alexander-Universität
Erlangen-Nürnberg (FAU), Haberstraße 9a, D-91058 Erlangen, monica.distaso@fau.de

Abstract

The problem of plastic accumulation in the environment requires the development of effective strategies to shift the paradigm of used plastics from wastes to resources. In the present contribution, after an overview of the current plastic management strategies, the possible role of nanotechnology to this emerging field is considered. In particular, the challenges related to the use of nano-additives to improve the properties of recycled plastics is discussed based on the fundamental aspects of colloid stabilisation. Finally, the contribution of nanotechnology to the fabrication of effective catalysts for the depolymerisation of plastics into the constituent monomers is outlined.

Keywords

nanoparticles; inorganic pigments; polymers; nanocomposites; packaging

Introduction

The images of the Great Pacific Garbage Patch have become the symbol of plastic pollution worldwide. An island of floating trash with an area three times larger than France and more than twice the size of Texas is located between California and Hawaii and contains around 79,000 tons of plastic debris [1]. The durability and low cost of plastic has made it a widespread material in everyday life, both in consumer and industrial products. Only packaging and single-use materials constitute 6.3 billion metric tons of plastic generated worldwide [2]. It has been estimated that between 4 and 12 billion of metric tons of plastics enters the ocean annually [2,3]. Traditional plastics do not undergo biodegradation, especially in the oceans, rather sunlight-promoted size reduction processes lead to the formation of so-called microplastics. These are tiny fragments of particles smaller than 5 mm, that due to their small size can easily be ingested by marine living organisms, and enter the biological nutrient cycle. Microplastics have been found in drinking water, kitchen salt and honey, through largely not yet understood mechanisms; remarkably, the effects of microplastics on the human health is not known [4]. Consequently, the European Community has set the ambitious target of ensuring that all plastic packaging is recyclable by 2030 under the roof of the circular economy [4,5] According to this concept, the traditional linear consumption model should be substituted by closed loops, where each product at the end of its life cycle can be re-transformed in the original product or in another useful one. In other words, the design of sustainable products shifted from the cradle-to-grave to cradle-to-cradle model, where ideally every material can be recycled infinite number of times [5].

Before analysing the possible contribution of nanotechnology to the field of circular economy of plastic materials, it is worth to chart a course of the current plastic management strategies.

Currently, plastic wastes undergo three main paths: landfill disposal, incineration and mechanical recycling. The landfill disposal has been recognised as less ideal solution for the waste management, in general, and more specifically for plastics. The accumulation of large amount of non-degradable plastic wastes over a limited area poses serious problems connected with the security of the sites and represents an economical loss of value products with a very short lifetime.

Incineration enables energy recovery from plastic wastes and has certainly some advantages with respect to landfill disposal, such as avoiding littering, leakages and accumulation in landfill. The value of only packaging plastics disposed in landfill and incineration has been estimated between 70 and 105 billion euro that are annually lost [4]. On the other hand, plastic materials are nowadays mainly synthesized starting from fossil fuels, therefore, their incineration to recover energy leads also to the formation of carbon dioxide, besides other gases,

contributing remarkably to the greenhouse gas (GHG) emissions. With the Paris Agreement, the European Community has committed to reduce the GHG emission by 2030 and become carbon neutral by 2050 [6,7]. To meet the challenge of GHG abatement and reduce the amount of plastic waste, the urge to move in the direction of a circular economy arises.

The third strategy of mechanical recycling of polymers is a viable route to reuse plastics over several cycles [8]. Following this approach, plastic materials at the end of their life cycles are envisaged not as wastes but as potential source of valuable products with properties (mechanical, optical) comparable to the pristine material. The mechanical recycling of polymeric materials appeared so far to be a feasible route from an operational and economical perspective. However, this route is at the same time an extremely challenging task: the presence of contaminants, including other polymer types, and the thermo-mechanical degradation of the polymers during the processing affect negatively the properties of the recycled material with respect to the original one. In fact, throughout the process chain from milling, melting and extrusion the properties of the polymeric materials are degrading due to the occurrence of physico-chemical phenomena such as thermo-mechanical oxidation and polymer chain scission under the action of radical formation, or upon hydrolysis. Consequently, a loss of the quality of the original products is observed.

A general strategy undertaken to compensate the loss in mechanical and optical properties of the recycled polymer is to mix it with virgin polymer in suitable proportions, usually not exceeding 10 wt. %. In this way, the new products introduced in the market contain a (relatively small) portion of recycled plastics and match the benchmark properties.

The challenges for the mechanical recycling of plastics are even more severe when the recycling of composite materials is targeted. Composite materials comprise several thin layers of structures closely connected with each other. As an example, aluminium is present in many packaging materials as a thin layer. Considering that bauxite, the mineral from which aluminium is extracted, has been recently enclosed in the list of critical raw materials from the EU community [9], the topic of composite recycling has become even more fundamental. The recycling of packaging materials accounts for only 9 % of the plastic generated worldwide in 2015 [4]. The co-presence of several polymeric materials, various coatings and adhesives, along with additives such as substances used during manufacturing (solvents and non-intentional impurities), oligomers and degradation products are among the technical reasons that limit to overcome this threshold [10].

Besides these traditional approaches of waste management, alternative routes are under developments. In a first instance, several efforts have been undertaken for the development of plastics that are produced from renewable raw materials and are, thus, classified as biobased plastics. Some relevant examples are poly-lactic acid (PLA) and poly-hydroxybutyrate (PHB), both synthesised from the fermentation of starch or glucose. Despite their promising biocompatible properties, these materials have not substituted the traditional plastic materials due to two major pitfalls: the competition with land for producing “crops for plastic” and the fact that the degradation process requires suitable experimental conditions (temperature, amount of oxygen, moisture, microorganisms) achievable only in dedicated composting plants. Therefore, if released into the environment they will not undergo biodegradation. Thus, it will be central in the near future to develop environmentally friendly materials, ideally able to degrade promptly and completely in non-harmful products under natural environmental conditions [11,12].

More recently, the concept of chemical recycling of polymeric materials has emerged as an intriguing approach to transform the polymeric materials into the corresponding monomers and/or into useful products for the chemical industry. In turns, the monomers can be reused to synthesise the virgin polymer with the same characteristics as the original starting material. The co-products besides the monomer shall be useful components to be fed into the market or to be used as chemical feedstock for further transformations in high added-value products. The guiding principle is therefore the atom economy: every atom that constitutes the waste material and the chemical educts used for their transformation into monomers shall be incorporated into useful chemicals, following the principle of green chemistry [13,14]. Therefore, the challenge is the design of materials and processes that enable the recycling of plastics, preserving their properties. While this approach is certainly promising, it requires an intensive research and development effort, especially for the identification of efficient, benign and recyclable catalysts able to realize the cradle-to-cradle transformation of plastic materials [13].

Table 1 summarizes the current strategies of plastic management and highlights advantages and disadvantages of each approach.

Table 1. Advantages and disadvantages of current approaches in plastic management

Approach	Short description	Advantages	Disadvantages
Landfill disposal	Wastes are accumulated in suitable locations	Release in the environment is avoided	High costs, risks management is required, polymers do not degrade spontaneously
Incineration	Plastic materials are combusted	Energy production	CO ₂ and other GHGs are generated, hazardous emissions, dependency on fossil fuels
Mechanical recycling	Comminution, melting and extrusion lead to new polymer	Polymers are reusable over a certain number of cycles	Loss of the mechanical and optical properties of materials
Biodegradable polymers	Materials derived from biomass	Good potential to GHGs abatement	Requires well-controlled conditions for the degradation
Chemical recycling	Depolymerisation reactions are carried out to obtain the monomers and useful co-products	The properties of the final polymer are maintained	Under development, requires efficient, cheap and reusable catalyst for the large scale application

In the end, the problem of plastic management remains and will most probably continue to be a scientific, economic and technological challenge also in the next decades. Besides an undeniable need to reduce the plastic consumption and its release into the environment, effective routes have to be developed to change the paradigm of plastic materials from wastes to resources.

In the current paper, the possible contribution of nanotechnology to the field of circular economy of plastic materials will be outlined. Namely, the use of nano-additives to improve the mechanical and optical properties of recycled materials and the development of nanocatalysts for the depolymerisation of plastics will be considered. Emphasis is given to the challenges related to the use of nanomaterials as plastic additives, considering the intrinsic thermodynamic instability of nanoparticles. Therefore, before considering the application of nanoparticles in this emerging field, it is worth to consider some fundamental concepts of nanoparticulate materials, in particular with respect to their colloidal stability.

What is nanotechnology?

Nanotechnology is defined as the ensemble of materials and techniques that are able to exploit new properties arising at nanoscale, whereby “nano” refers to the size of 10⁻⁹ meters (nm). Nanomaterials are defined as objects that have at least one dimension smaller than 100 nm. It has been observed that materials in this size regime display unique properties, which make them clearly different from their bulk counterpart. Examples of these changes in material properties are the reduced values of melting point, the tuneable optical properties of semiconductors in the quantum size regime and the magnetic properties, to mention only a few.

For the purpose of this contribution, it is worth to focus the attention on three fundamental aspects of nanoparticles: the dispersability, biocompatibility and their catalytic properties.

Particles are surface determined solids where size distribution, shape and surface stabilisers define their properties, functionality and stability over time. The size and shape of particles can be tuned precisely at atomic level using state of the art advanced liquid phase synthesis. However, interfaces play a major role in providing stability over time and functionality. Nanoparticles are kinetically stable objects. Therefore, in the absence of an effective stabilisation their tendency to undergo aggregation and ripening is an underlying phenomenon that has to be always taken into account. In every application that makes use of nanoparticles, it is important to ensure

the absence of aggregation and agglomeration by exploiting three major stabilisation routes (Figure 1). The steric stabilization makes use of organic ligands adsorbed onto the particles surface either during the synthesis of nanomaterials, or in a post-synthetic step. In electrostatic stabilization, charged species are adsorbed onto the surface of particles, providing sufficient electrostatic repulsion. In electro-steric stabilization, charged organic molecules comprise the steric and electrostatic effect. Usually, zeta-potential values larger than ± 30 mV are used as guidelines to define if a particle suspension is stable.

Derjaguin-Landau-Verwey and Overbeek (DLVO) theory, initially developed for planar charged surfaces, provides an excellent framework to model the interactions between charge-stabilized nanoparticles [15]. This approach, however, breaks often down at the lower nanoscale, where for instance ion specific forces between colloidal particles cannot be explained quantitatively [16].

Figure 1 summarizes the main stabilisation approaches of nanoparticles and their dispersability in media with various polarity, being the last both solid (polymers, resins, plastics) and in liquid state (solvent, oil, etc.).

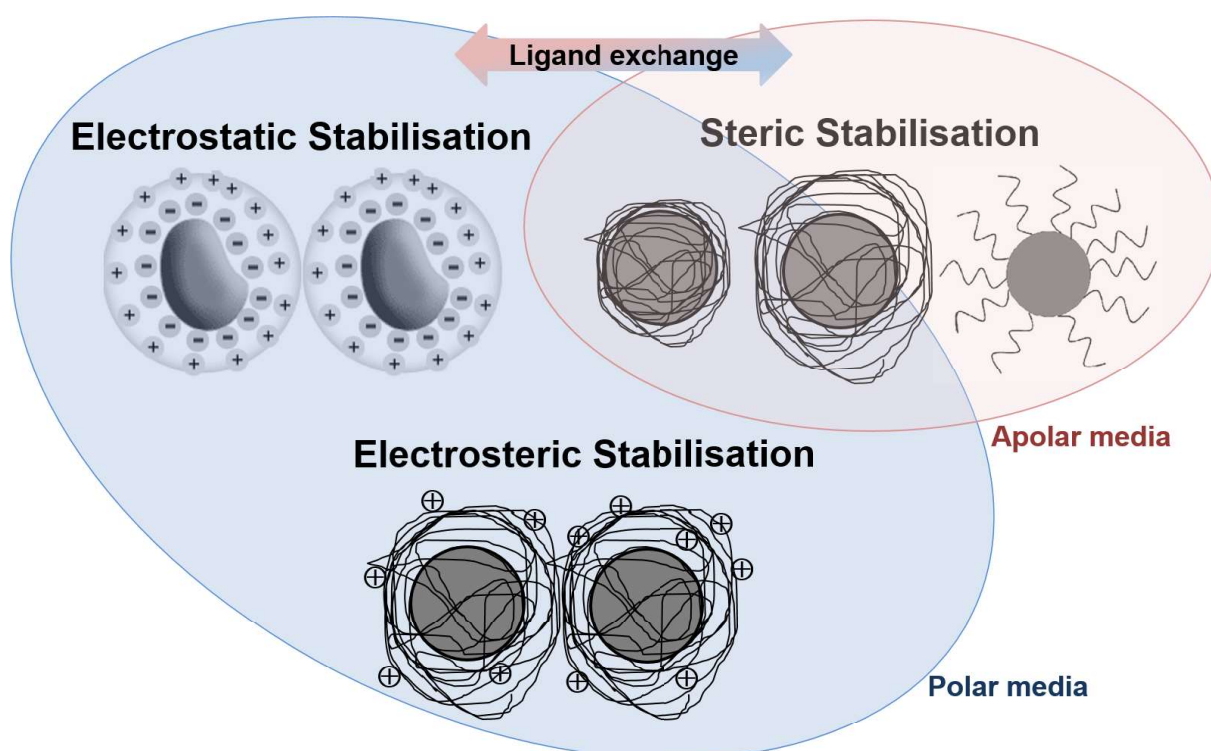


Fig. 1. Overview of the principle approaches for the stabilisation of nanoparticles in media with various polarity.

The surface functionalisation needs to be adapted to the target application. In particular, the selection of suitable ligands will define the dispersability of particles in media with various polarity. Accordingly, short and polar chain ligands and ionic species will be suitable to stabilise nanoparticles within polar media ($\epsilon > 50$), whereas the stabilisation in organic solvents with intermediate polarity ($\epsilon = 20 \div 50$) and apolar matrices ($\epsilon < 20$) will require the use of long-chain surfactants.³ In some applications, it might be necessary to disperse the (nano)particles in solvents or, more general, in matrices with a dielectric constant very different from the medium where the synthesis of nanoparticles was carried out. For example, the shape and size of semiconductor nanocrystals can be precisely engineered in solvents with low dielectric constant and in the presence of long chain surfactants (i.e. oleylamine, oleic acid, tri-octyl-phosphine, and tri-octyl-phosphine oxide) that make them dispersible only in apolar solvents (i.e. chloroform, hexane, toluene). Several methods are available in the scientific literature to carry out ligand exchange processes. These methodologies enable the substitution of long chain surfactants with short chain ligands [17], or even with metal ions and complexes [18]. Also, the opposite is possible: particles synthesized in polar environment, can be re-dispersed in apolar media by

³ ϵ is the dielectric constant

realizing a steric stabilisation. In all case, the molecules adsorbed onto the particle surfaces will have to be able to create sufficient repulsive forces between particles, to keep them apart and prevent aggregation and agglomeration. Only the colloid stability will ensure the durability of the functional material.

A second aspect that needs to be considered when the application of nanoparticles in large consumer products is envisaged is the potential toxicity of nanomaterials for human and the environment. While there are several studies in the literature devoted to the assessment of particle toxicity, the results are not conclusive [19]. Therefore, it is important to carry out studies on the transport of nanomaterials within the solid matrices and devices where they are incorporated in order to ensure that they are not released to the external environment. Finally, the application of nanomaterials in the field of catalysis has generated remarkable breakthrough in the last decades [20]. The enhanced activity and the size- and shape- dependent properties are ascribed to the majority of atoms residing onto the particles surface, rather than in the bulk. In heterogeneous catalysis, the use of nanoparticles has led to enhancement of catalytic activity as a trade-off between kinetic and thermodynamic aspects of adsorption on the increased number of active sites on the surface, and desorption of products from particles surface. In photocatalysis, semiconductor particles can be designed to have suitable bandgap and combined to harvest sunlight over a wide range of wavelengths. In electrocatalysis, the influence of particle size, structure and catalyst support is well-recognised [21]. Through the engineering of particles synthesis, it is possible to maximise the exposure of high index crystalline facets that notably bear the highest concentration of defects.

In general, the catalyst support has to be understood not as a neutral observer of the catalytic reactions, but as a key actor defining, together with the catalyst, the kinetics and thermodynamics of the catalytic processes [22]. The deposition of nanoparticles onto suitable catalytic supports is a key strategy to recycling and reusing the catalysts, which is usually a very expensive component.

Nanoparticles as additives in plastic materials

With the current scenario, the most practical approach for a short-term reduction of the amount of plastic released in the environment seems to be the mechanical recycling.

As shortly mentioned in the introduction, the mechanical recycling of plastic materials requires the addition of various amount of virgin polymer to balance the loss of mechanical strength and the degradation of the optical properties in order to give access to polymeric materials with benchmark properties over an infinite number of cycles.

Recently, it has been shown that a valuable alternative to the use of virgin polymer to enhance the mechanical and optical properties of the recycle polymer is the addition of nanofillers as additives with the purpose to push forward the reuse and the recycling of plastics [23]. This strategy has been applied to several polymeric materials, such as polyethylene terephthalate (PET), polystyrene (PS), polyethylene and high-density polyethylene (PE and HDPE), polypropylene (PP), etc.

The nano-additives that can be potentially used are classified as organic and inorganic materials. The former comprise carbon-derived components such as graphene, carbon nanotubes and nanohorns, or nanocellulose. Interestingly, several of these carbon-based materials can be nowadays derived from biomass [24, 25]. Among the inorganic nano-additives, metal oxide materials such as ZnO, TiO₂ and SiO₂ nanoparticles have found already applications in the recycling of poly(ethylene terephthalate), polypropylene and polystyrene mainly as inorganic nano-reinforcement to improve the mechanical properties [26-28].

Clays are also widely used as additives in recycled plastics, as they are particularly effective in increasing the yield stress, the modulus of tension, rigidity, hardness, and resistance to humidity [23,29,30].

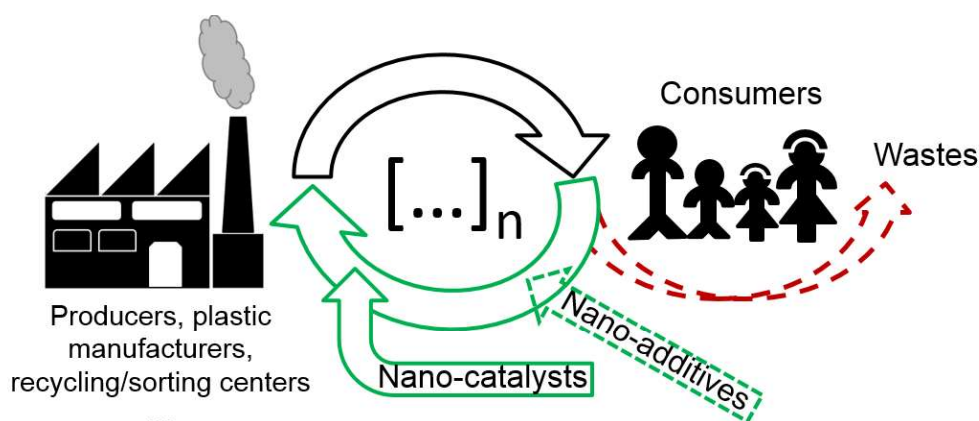


Fig. 2. General scheme of the life cycle of plastic materials from producers to consumers, and possible path alternative to the waste generation, from consumers to recycling/sorting centres and plastic manufacturers, involving the contribution of nanotechnology.

In the examples provided above the inorganic materials are usually used in small amount, in a way that they compensate the lack of mechanical strength, while maintaining a neutral colour with respect to the original material. However, nanoparticles could be used also as nano-pigments, whereby in the framework of this application they are providing beside the nano-reinforcement function also an optical response such as the colour. The colour of the original matrix can be enhanced, intensified or modified, accordingly. This approach would be particularly interesting in the cradle-to-cradle perspective, where the plastic material derived from a recycling process can find application not only in the original product but also in a new one.

Following this idea, inorganic nanoparticles can be classified based on their optical response as ultraviolet (UV), UV-visible and UV-visible-near infrared (NIR) pigments. In the first class, white solids are enclosed such as silica, TiO_2 , ZnO . Among the visible pigments, iron oxides can play a central role for the strength of the colour that they are able to provide and for the biocompatibility of this class of materials. Accordingly, hematite is an example of a red pigment, goethite is yellow and magnetite/maghemite are black pigments. In the NIR region, pigments can be used to exploit thermal management applications. However, the use of nanoparticles as additives in plastic to enhance the mechanical and optical properties of recycled polymers requires still extensive studies at several levels.

The majority of nano-additives available in the market are synthesised on industrial scale either in gas-phase processes or in liquid phase using usually water as solvent. The pigments obtained are available as dried solids that need to be re-dispersed in order to be used in a given application. This re-dispersion in liquid or molten media requires a careful control of the solid-liquid interfaces over a wide range of temperatures by applying the strategies outlined in Fig. 1. In order to ensure a homogeneous distribution of the particles inside the recycled plastic, it is fundamental to match the polarity of the functional groups onto the particles surface with the polarity of the matrix. This approach ensures an even distribution of the nanoparticles in the organic matrix, where the presence of particles as single objects and not as aggregates is fundamental in order to ensure that the properties of particles are transferable to their ensemble.

In order to realise processes with a true environmental and economic benefit, it is necessary to ensure that the composite material obtained after the addition of the nano-additives at the first cycle, can be recycled over several cycles maintaining the same properties. This is true not only for the organic matrices, but also for the nano-additives. In other words, the stability of particles and their dispersibility has to be ascertained to ensure that the particles will not undergo aggregation and/or ripening in the successive cycles. A second important point is how to ensure that the nanoparticles remain enclosed in the plastic material and are not released in the environment. There, besides the direct potential risks for living organisms to get in contact with nanoparticulate systems of which the toxicological properties are not yet ascertained, the accumulation of non-degradable nanoparticles in the environment would indirectly threaten human health, similarly to the phenomenon of microplastics described above. If these critical points are not addressed, the applicability of nanoparticles as additives for the processing of post-consumer plastics in the framework of a circular economy seems very labile (dashed green arrow in Fig. 2).

Nanoparticles as catalysts for the depolymerisation of plastics

Instead, the depolymerisation of plastics in the constituent monomers appears to be a more promising research field. For a comprehensive overview of the state of the art in materials and processes, the reader is invited to read the recent contribution by Sheldon and Norton [14]. In the following, it will be proposed how nanotechnology can make a breakthrough in this nascent field (Table 1).

With their high surface area, the possibility to tune the reactivity by controlling the size and shape of the nano-architecture and defect density, nanoparticles have been reported as active catalysts in a number of processes. The application of nanoparticles as catalysts is one of the few fields where nanotechnology has reached a market application (see for instance the catalytic converter and fuel cells). In the specific case of catalysts for plastic depolymerisation, the state of the art is still at lab-scale and can be considered at its infancy. The key challenges are here the effective immobilisation of nanoparticulate catalysts onto suitable catalytic supports in a way that the activity of the catalyst is enhanced through a cooperative effect with the substrate. Besides the enhanced activity of particles due to the large surface to volume ratio, the possibility to fabricate multifunctional materials is a clear advantage of nanotechnology. A multifunctional material comprise several domains spatially and electronically organised onto the substrates. The domains can interact with each other, or carry out subsequent steps of a complex chemical transformation. Deactivation processes such as Ostwald ripening, detachment of the particles from the catalytic support with consequent dissolution and Ostwald ripening have to be circumvent. These challenges can be tackled by strengthening the interaction of the nanocatalysts with the solid support and by exploiting encapsulation strategies in porous shell. The size of the pores has to be large enough to enable the access of the polymer to the active sites of the catalysts, and small enough with respect to the particles size to ensure that the nanoparticulate catalysts remain protected inside the porous shell.

Another important contribution of nanotechnology to the depolymerisation of plastics is the possibility to recover and reuse the catalysts over several cycles. A possible strategy to achieve the recyclability is to immobilise the catalysts onto the surface of superparamagnetic particles. These are highly crystalline materials that, in the absence of an applied field, behave as non-magnetic, but when a magnetic field is applied they are strongly attracted to the external magnet and can be separated from the solution by magnetic decantation [31]. The magnetic decantation is well-know not only at lab scale, but also in some industrial segments. Examples of superparamagnetic particles are Fe_3O_4 (magnetite) and CoFe_2O_4 (cobalt ferrite), for which water-based protocols for the largescale production are available.

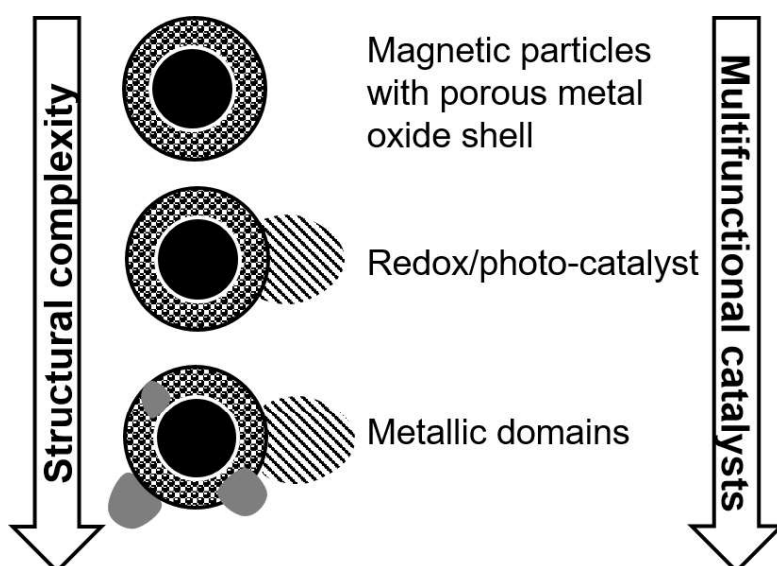


Fig. 3. Nanotechnology offers the theoretical framework for the fabrication of multifunctional materials.

Impact

Plastic materials have influenced largely the modern society with durable, light and flexible products. The non-degradable properties of plastics is of paramount importance in order to provide robustness and durability of plastic materials, but at the same time it leads to their accumulation in the environment, often under the form of microplastics that originate from photodegradation of macroscopic materials. However, the problem of plastic accumulation in the environment needs to be solved at a global level. For decades, higher income countries have exported plastics to lower income countries of the East Asia and Pacific area. However, the Chinese ban to the import of plastics from other countries poses serious challenges to the source lands that have to find an alternative to landfill and incineration [32].

Recently, waste management based on plastic recycling has gathered remarkable attention in the scientific community in both industry and academia. The recycling of plastics has important impacts on environmental, economic and social level. The plastic recycling and the development of biodegradable plastic materials is expected to have a very positive impact on the GHG abatement and will help Europe to keep the commitment to the Paris agreement. This target, however, will be achieved only if true sustainable products will be developed with environmental, social and economical benefits throughout the entire process chain, from extraction of raw materials to disposal of the final wastes.

Industry has recognized the importance of shifting the paradigm of used plastics from wastes to resources. However, it is very unlikely that the plastic recycling and the reduction of the plastic wastes released in the environment can be successful without a direct involvement of the citizens. The separation of household plastic wastes has to be pushed forward in order to ensure the homogeneous composition of the feed before recycling. This is a priority both for the mechanical recycling of plastics and becomes fundamental for their chemical depolymerisation into constituent monomers. The combination of life cycle assessment and cradle-to-cradle principles is necessary in order to quantify and design general rules for the development of materials and processes that are more sustainable for human and the environment [33]. A realistic perspective on the cradle-to-cradle paradigm from an energetic point of view should not be neglected [34]. What is clear and widely accepted is that the release of plastics in the environment, either traditional or degradable, virgin or recycled, is not anymore an acceptable solution.

Conclusions

In summary, it has been shown that nanotechnology can contribute to the field of waste management. Nanoparticles can be used as additives for mechanically recycled plastics to improve the mechanical and optical properties. Another possible contribution of nanotechnology is the development of nanoparticulate catalysts for the depolymerisation of plastic into the constituent monomers. For this purpose, the nanocatalysts have to be immobilised onto the surface of suitable carriers, whereby recoverable magnetic materials are an example of possible catalytic support. In both kind of applications, it is fundamental not only to control the size and shape of nanomaterials, but especially the surface properties of the nanoparticles. They will contribute in large scale to determine the dispersability of particulate additives in media with various polarity, the strength of interaction between the nanocatalysts and the catalytic support, and ultimately the catalyst performance.

Conflict of interest

There are no conflicts to declare

References

- [1] <https://www.nationalgeographic.com/news/2018/03/great-pacific-garbage-patch-plastics-environment/>, National geographic.
- [2] Geyer R, Jambeck JR, Law KL. Production, use, and fate of all plastics ever made. *Science Advances* 3 (2017), e1700782.
- [3] Jambeck JR, Geyer R, Wilcox C, Siegler TR, Perryman M, Andrady A, Narayan R, Law KL. Marine pollution. Plastic waste inputs from land into the ocean. *Science (New York, N.Y.)* 347 (2015), 768–771.
- [4] European Community, <https://ec.europa.eu/environment/circular-economy/pdf/plastics-strategy-brochure.pdf>.
- [5] World Economic Forum, Ellen MacArthur Foundation and McKinsey & Company, *The New Plastics Economy — Rethinking the future of plastics* (2016, <http://www.ellenmacarthurfoundation.org/publications>).
- [6] DG CLIMA - DG Climate Action, COM(2015)81/F1 - EN.
- [7] DG SG - Secretariat-General, COM(2016)110/F1 - EN.

- [8] Schyns ZOG, Shaver MP. Mechanical Recycling of Packaging Plastics: A Review. *Macromolecular Rapid Communications* (2020), e2000415.
- [9] European Community, https://ec.europa.eu/growth/sectors/raw-materials/specific-interest/critical_en.
- [10] Groh KJ, Backhaus T, Carney-Almroth B, Geueke B, Inostroza PA, Lennquist A, Leslie HA., Maffini M, Slunge D, Trasande L, Warhurst AM, Muncke J. Overview of known plastic packaging-associated chemicals and their hazards. *The Science of the Total Environment* 651 (2019), 3253–3268.
- [11] Garcia JM, Robertson ML. The future of plastics recycling. *Science (New York, N.Y.)* 358 (2017), 870–872.
- [12] Zhu J-B, Watson EM, Tang J, Chen EYX. A synthetic polymer system with repeatable chemical recyclability. *Science (New York, N.Y.)* 360 (2018), 398–403.
- [13] Hong M, Chen EYX. Chemically recyclable polymers: a circular economy approach to sustainability. *Green Chemistry* 19 (2017), 3692–3706.
- [14] Sheldon RA, Norton M. Green chemistry and the plastic pollution challenge: towards a circular economy. *Green Chemistry* 22 (2020), 6310–6322.
- [15] Israelachvili JN. *Intermolecular and Surface Forces*, 3rd ed., Elsevier Science, Saint Louis, 2015.
- [16] Parsons DF, Boström M, Lo Nostro P, Ninham BW. Hofmeister effects: interplay of hydration, nonelectrostatic potentials, and ion size. *PCCP* 13 (2011), 12352–12367.
- [17] Sperling RA, Parak WJ. Surface modification, functionalization and bioconjugation of colloidal inorganic nanoparticles. *Philosophical Transactions. Series A, Mathematical, Physical and Engineering Sciences* 368 (2010), 1333–1383.
- [18] Nag A, Kovalenko MV, Lee JS, Liu W, Spokoyny B, Talapin DV. Metal-free inorganic ligands for colloidal nanocrystals: S²⁻, HS⁻, Se²⁻, HSe⁻, Te²⁻, HTe⁻, TeS₃(²⁻), OH⁻, and NH₂⁻ as surface ligands. *Journal of the American Chemical Society* 133 (2011), 10612–10620.
- [19] Nel A, Xia T, Meng H, Wang X, Lin S, Ji Z, Zhang H. Nanomaterial toxicity testing in the 21st century: use of a predictive toxicological approach and high-throughput screening. *Accounts of Chemical Research* 46 (2013), 607–621.
- [20] Heiz U. (Ed.), *Nanocatalysis: With 14 tables*, 2nd ed., Springer, Berlin, 2008.
- [21] Hayden BE. Particle size and support effects in electrocatalysis. *Accounts of Chemical Research* 46 (2013), 1858–1866.
- [22] Rodriguez JA, Liu P, Hrbek J, Evans J, Pérez M. Water gas shift reaction on Cu and Au nanoparticles supported on CeO₂(111) and ZnO(0001): intrinsic activity and importance of support interactions. *Angewandte Chemie (International ed. in English)* 46 (2007), 1329–1332.
- [23] López de Dicastillo C, Velásquez E, Rojas A, Guarda A, Galotto MJ. The use of nanoadditives within recycled polymers for food packaging: Properties, recyclability, and safety. *Comprehensive Reviews in Food Science and Food Safety* 19 (2020), 1760–1776.
- [24] Jagadeesan D, Eswaramoorthy M. Functionalized carbon nanomaterials derived from carbohydrates. *Chemistry, an Asian Journal* 5 (2010), 232–243.
- [25] Gu D, Ma R, Zhou Y, Wang F, Yan K, Liu Q, Wang J. Synthesis of Nitrogen-Doped Porous Carbon Spheres with Improved Porosity toward the Electrocatalytic Oxygen Reduction. *ACS Sustainable Chemical Engineering* 5 (2017), 11105–11116.
- [26] Mallakpour S, Javadpour M. The potential use of recycled PET bottle in nanocomposites manufacturing with modified ZnO nanoparticles capped with citric acid: preparation, thermal, and morphological characterization. *RSC Advances* 6 (2016), 15039–15047.
- [27] Herrera-Sandoval GM, Baez-Angarita DB, Correa-Torres SN, Primera-Pedrozo OM, Hernández-Rivera SP. Novel EPS/TiO₂ Nanocomposite Prepared from Recycled Polystyrene. *Material Science and Applications* 4 (2013), 179–185.
- [28] Hadi NJ, Mohamed DJ. Study the Relation between Flow, Thermal and Mechanical Properties of Waste Polypropylene Filled Silica Nanoparticles. *Key Engineering Materials* 724 (2016), 28–38.
- [29] Velásquez E, Garrido L, Valenzuela X, Galotto MJ, Guarda A, López de Dicastillo C. Physical properties and safety of 100% post-consumer PET bottle -organoclay nanocomposites towards a circular economy. *Sustainable Chemistry and Pharmacy*, 17 (2020) 100285.
- [30] Farshchi N, Ostad YK. Sepiolite as a nanofiller to improve mechanical and thermal behavior of recycled high-density polyethylene. *Progress in Rubber, Plastics and Recycling Technology* 36 (2020), 185–195.
- [31] Rossi LM, Costa NJS, Silva FP, Wojcieszak R. Magnetic nanomaterials in catalysis: advanced catalysts for magnetic separation and beyond. *Green Chemistry* 16 (2014), 2906–2933.

- [32] Brooks AM, Wang S, Jambeck JR. The chinese import ban and its impact on global plastic waste trade. *Science Advances* 4 (2018), eaat0131.
- [33] Bakker CA, Wever R, Teoh C, de Clercq S. Designing cradle-to-cradle products: a reality check. *International Journal of Sustainable Engineering* 3 (2010), 2–8.
- [34] Skene KR. Circles, spirals, pyramids and cubes: why the circular economy cannot work. *Sustainability Science* 13 (2018), 479–492.