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CRITICAL REVIEW

Industrial applications of immobilized nano-biocatalysts

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Abstract

Immobilized enzyme-based catalytic constructs could greatly improve various industrial processes due to their extraordinary catalytic activity and reaction specificity. In recent decades, nano-enzymes, defined as enzyme immobilized on nanomaterials, gained popularity for the enzymes' improved stability, reusability, and ease of separation from the biocatalytic process. Thus, enzymes can be strategically incorporated into nanostructured materials to engineer nano-enzymes, such as nanoporous particles, nanofibers, nanoflowers, nanogels, nanomembranes, metal–organic frameworks, multi-walled or single-walled carbon nanotubes, and nanoparticles with tuned shape and size. Surface-area-to-volume ratio, pore-volume, chemical compositions, electrical charge or conductivity of nanomaterials, protein charge, hydrophobicity, and amino acid composition on protein surface play fundamental roles in the nano-enzyme preparation and catalytic properties. With proper understanding, the optimization of the above-mentioned factors will lead to favorable micro-environments for biocatalysts of industrial relevance. Thus, the application of nano-enzymes promise to further strengthen the advances in catalysis, biotransformation, biosensing, and biomarker discovery. Herein, this review article spotlights recent progress in nano-enzyme development and their possible implementation in different areas, including biomedicine, biosensors, bioremediation of industrial pollutants, biofuel production, textile, leather, detergent, food industries and antifouling.

Keywords Nanoenzymes · Nanocatalysis · Protein stability · Nanomaterials · Industrial applications

Abbreviations

CNTs	Carbon nanotubes
ChOx	Cholesterol oxidase
GONS	Graphene oxide nanosheets
GOx	Glucose oxidase
HRP	Horseradish peroxidase
MNPs	Magnetic nanoparticles
MWCNTs	Multi-walled carbon nanotubes
NBC	Nanobiocatalytic
NBT	Nanobiotechnology
NC	Nanocomposite
NEs	Nanoenzymes
NM	Nanomaterial
NPs	Nanoparticles
PEG	Polyethylene glycol
PLGA	Polylactic–polyglycolic acid
PS	Polystyrene
SOD	Superoxide dismutase

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Introduction

Since the 1960s, the development of immobilized enzymes for efficient bio-catalysis has become a fascinating research topic, especially due to its reusability potential if the enzyme retained its catalytic properties [1, 2]. Immobilization transforms the enzyme from a homogeneous catalyst into a heterogeneous one, allowing its easy handling and repeated use in batch processes and the possibility of decoupling biocatalysts in continuous processes from the residence time [3]. Enzyme immobilization is essential for a number of biomedical, biotechnological and industrial applications. The goal is to stabilize and re-use the biocatalyst even in unsuitable surroundings (i.e., high temperatures or wide pH ranges, high concentrations of substrate, and non-aqueous solvents) [4].

A number of immobilization processes have been established to date, with each enzyme having its own unique support matrix and preferable procedure and conditions [2, 3]. Some of these processes include the protein modification by polymer chains, followed by adhesion, covalent binding and entrapment, and have been well established and deployed using various support matrices [5, 6].

The extensive progress of nanotechnology is followed by the rapid growth of a new field called "nanobiotechnology (NBT)", allowing for new possibilities for the industrial applications of enzymes. Nanomaterials (NMs) have high specific surface areas and their own unique, exciting features, including physical, magnetic, spectroscopic, electrical, and chemical properties [7, 8].

The generation of NBT is based on the fusion of nanotechnology and biotechnology with possible synergistic benefits. Thus, an array of enzymes has been immobilized onto numerous NMs through conventional approaches, e.g., adsorption and covalent attachment/linking, etc. [9–11]. The advantageous features of nanostructured materials include nanopore and NP size, optimized nanofiber or nanotube diameter [12, 13], conductivity and magnetism. NMs can be prepared with uniform size distribution, which is comparable to enzyme molecules. They revolutionized the concept of nano-bio-catalysis (NBC) in various areas of biotechnology, leading to improved catalytic properties, stability, and reusability [14–16]. Keeping the above key points in mind, we reviewed potential applications of nano-enzymes (NEs) in various industrial applications [1, 17]. More specifically, the applications in different fields, including food industry, biosensing, medicine, sewage water treatment, antifouling and detergent manufacturing, proteomic analysis, and biofuel manufacturing, have been discussed with suitable examples [1, 18–22] (Fig. 1).

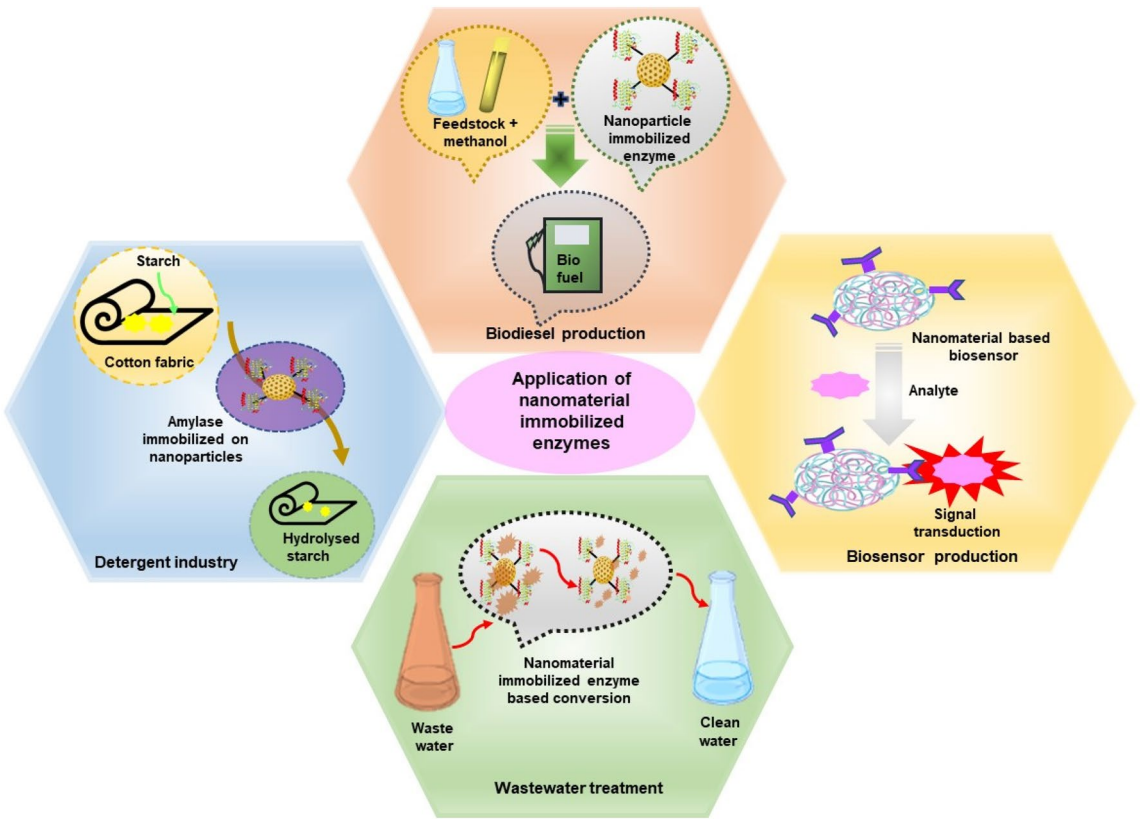

Fig. 1 Nanomaterials were applied as appropriate tools for different applications due to their many distinctive morphological and structural qualities

Stability, structure and function of NEs

The fast growth of nanotechnology has substantially improved the chance of interaction between enzymes and NMs, thus leading to novel NEs [23–25]. Indeed, NMs fulfill many 'ideal' prerequisites for enzyme immobilization [26–31]. For example, due to their high surface to volume ratio, they show improved binding efficiency, often leading to hyperstability of macromolecules, and might improve the performances of enzymatic systems. These NEs can be found in a broad spectrum of applications, including diagnostics, sensing, and drug delivery (Fig. 2). Moreover, the development of biocompatible materials with specific functions has been reported [2, 3, 32–35]. Several enzyme models, including lipase, laccase, xylanase, lysozyme, horseradish peroxidase (HRP), catalase, and trypsin, were adsorbed firmly onto organic and inorganic NPs [36–41]. Enzyme immobilization on NMs can substantially improve the enzyme's catalytic properties in accordance with fine-tuning and rational design [36, 37, 42]. Indeed, in many cases the understanding of surface properties of the selected protein and the nanomaterial leads to highly active nano-bioconjugates [43]. Nevertheless, efforts of manufacturers can be frustrated by adverse effects of nanomaterials on biological macromolecules.

A number of enzymes have specific primary, secondary and tertiary structures, which result in suitable engagements with NPs and NMs. Indeed, the interaction between proteins and nanomaterials, besides covalent binding through molecular spacers and non-specific physical adsorption, can be obtained by molecular recognition that depends on both the structure of the specific protein (primary, secondary and tertiary structures) and the surface features (material nature and size, density and distribution of functional groups) of the selected nanomaterial [44]. In favorable cases, a highly active and very stable nano-bioconjugate can be obtained [43, 45]. Nonetheless, the orientation of enzymes towards NPs and NMs is critical and should be considered with care prior to perform their immobilization. This is to partially, or entirely, prevent potential blockage or hindrance of the enzyme active site [46]. Moreover, also the physical and chemical characteristics of NMs and reaction conditions (e.g., solvents, temperature and pH) may influence the binding of enzymes, their stability and substrate availability [47, 48]. Notably, in several cases the immobilization on NMs improves enzyme stability against thermal treatments or denaturing agents, such as sub-optimal pH or harsh chemicals [14, 49, 50]. Moreover, the size of NPs could influence the interaction between enzyme and its supporting matrix, thus modulating the function of bound enzymes. For the purpose of distinguishing size impacts from other factors, various-sized silica NPs (SNPs) (4, 15 and 35 nm) have been experimented for effects on structure, thermodynamic and kinetic durability of cytochrome c (cyt c) [51]. Specifically, authors observed that the structure and stability of cyt c was gradually affected at increasing the size of silica NPs, leading to a modification of the heme microenvironment.

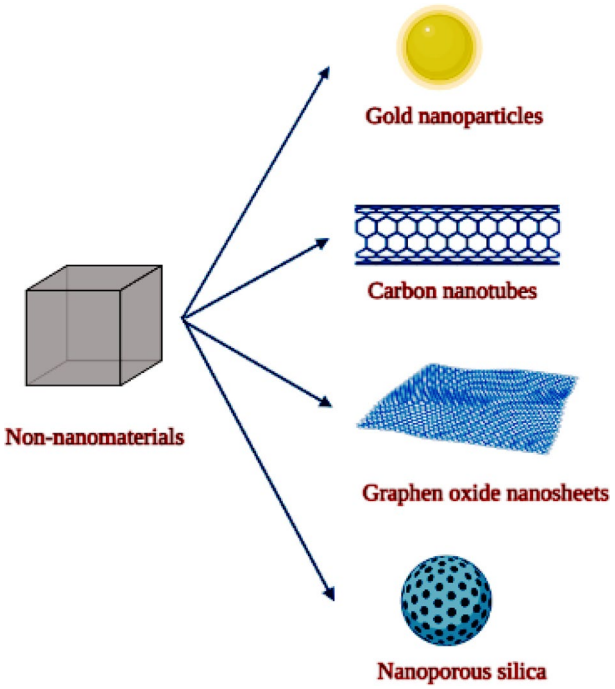

Fig. 2 Schematic representation of large surface of nanostructured materials compared to non-nanomaterials

NEs for biosensor applications

NEs-based biosensing constructs require a detector, connected to a biological sensing element, to detect an analyte. This detector converts the physicochemical transformation produced by the biological component into a measurable signal correlated to analyte concentration [2, 3, 52–54]. Enzymes are the most common biological components used for biosensor development. In the case of the signal-transducing format, NEs-based sensors consists of four main groups, i.e., (1) electrochemical, (2) optical, (3) piezoelectric, and (4) calorimetric devices [53, 55]. Enzyme-based biosensors generally show good sensitivity, rapid response, resistance against electrical and magnetic disturbances, geometric versatility, size attribution at micro- and nanoscale, low-cost and lightweight, and can provide alternatives to laboratory-based sensing benchtop instrumentation [56, 57]. Several NPs have been used for enzyme immobilization in biosensors development, as

listed in Table 1. From a general standpoint, NPs present a large surface area at the material interface and thus support enzyme binding with high loading capacity, which ultimately can lead to enzyme stabilization by fixing its structural conformation [52, 58, 59]. Further, the capability to modify NMs suggest excellent potential for improving the performance of NEs-based sensors [6, 14, 60]. Besides, NPs made of noble metals, such as gold, silver and platinum, can significantly increase the electrical conductivity of the electrode's immobilized enzyme layer, leading to both improved sensitivity and rapid detection in the case of electrochemical biosensors [61, 62]. Moreover, noble metal NPs can act as catalysts for electrochemical reactions, such as the typical redox catalysis of H_2O_2, as observed in the construction of glucose biosensors based on gold NPs [63–65]. Other NMs can provide an electrocatalytic support for enzyme binding, such as iron oxides [66, 67], and different biosensors were developed [68–70]. Moreover, several electrocatalytic magneto-switchable biosensors have been developed using a combination of macromolecules (enzymes and antibodies) and magnetic iron oxide-based NPs or other materials, such as carbon nanotubes (CNTs), electroconductive polymers, chitosan, and so on [71–76]. Several biosensor devices comprising numerous enzymes, e.g., lipase, glucose oxidase (GOx), peroxidase, urease, cholesterol oxidase (ChOx), penicillin acylase, and different NPs have been extensively applied in different sectors, including biomedical, clinical settings, environmental recognition, food analysis, and pharmaceutical analysis [52, 62, 77, 78]. Examples of enzyme-based biosensor devices associated with nanomaterials can be found in Table 1. Notably, in many cases the use of enzymes immobilized to NPs for biosensing can amplify their analytical performances and dynamic parameters, leading to reduced response time and increased sensitivity. However, this is not a general behavior, and biosensor development should be evaluated case by case [52, 62, 63, 71, 77]. In any case, the development of the biosensing device should be optimized according to the specific industrial application requirements, in terms of limits of detection, sensitivity, dynamic range, response time and operative conditions.

NEs for biofuel production

Recently, investigations on biofuels have received significant recognition, because of the raise of public interest for renewable energies aimed at replacing environmentally harmful fossil fuels. Biofuel production involving enzymes also rapidly grew due to the observed high conversions and fast reaction rates [79–84].

Among biofuels, biodiesel is a blend of mono-alkyl esters derived from the transesterification of natural long-chain fatty acid esters with low molecular weight alcohols. Natural triglycerides, usually vegetable oils, have been utilized for large-scale biodiesel production with the wide application of lipases. Cellulases have also been used for biofuel production, in this case for the production of ethanol by glucose fermentation [85, 86]. It was observed that the immobilization on NPs can prevent the low stability of enzymes in complex environments, and also allowed their reusability, with the further advantage of improving the flexibility of reactor design. In this view, size, shape, surface properties and chemical nature are important parameters for the application of nanomaterials as support for enzyme immobilization. Once prepared, these nano-enzymes can be used for a variety of industrial processes. In this context, the separation from the reaction mixture for further re-utilization represents one of the most important advantages with respect to soluble enzymes as recyclability can lead to a significant reduction of the process cost. With the exception of magnetic nanomaterials, characterized by the obvious magnetic drivability by magnetophoresis [87], approaches adopted for separating nano-enzymes from the reaction mixture are generally based on selective filtration, density gradient centrifugation, gel permeation chromatography and field flow fractionation. Sedimentation and centrifugation represent the most convenient solutions for industrial-scale nano-enzyme isolation, even if the final result depends on the density difference between the nanomaterial and the solvent. Nevertheless, the specific technique is still being trialed and challenges remain for large-scale operations [88].

Cellulases immobilized on silica [89, 90] and magnetic NPs (MNPs) have been successfully used to hydrolyze cellulose to obtain fermentable sugars for biofuel (ethanol) production [83]. Examples of nano-enzymes applied for biofuel production are reported in Table 2.

Typically, cellulases immobilized on MNPs demonstrated high thermostability (up to 80 °C), long half-life, efficient recovery, and reusability [83]. Based on a literature report, three different types of cellulases immobilized on gold-coated magnetic silica NPs enabled the single-step hydrolysis of complex cellulose starting materials in order to generate biofuel [91]. Magnetic cross-linked enzyme aggregates (mCLEAs), created by cross-linking a mixture of lipases covalently bound to magnetic NPs, were able to convert (80–85%) different vegetable oils (from olive, microalgal, non-edible vegetables or cooking waste) to substrates for biodiesel production [84]. Gold NPs were applied for the non-covalent immobilization of enzymes, facilitating the regeneration of deactivated bioreactors [92]. CNTs, graphene oxide nanosheets (GONS) and magnetic multi-walled carbon nanotubes (MWCNTs) were also reported for the

Table 1 Examples of enzymes immobilized on nanoparticles (NPs) and applied for the development of biosensors

Immobilized enzyme	Type of NP	Application	References
Glucose oxidase	Se NPs	Biosensor for the determination of glucose in body fluids, food and agricultural products	[189]
Uricase	ZnO NPs	Uric acid biosensor in serum	[190]
Glucose oxidase	Au NPs	Catalytic nanodevice to construct nanoreactors	[181]
Laccase	Bare and zinc-tetra-aminophthalocyanine-Fe_3O_4–SiO_2) NPs	Fiber optic biosensor for catechol and bisphenol A	[191–193]
Glucose oxidase	NiO NPs	Amperometric biosensor for glucose	[194]
Glucose oxidase	Pt and Au NPs	Naked eye detection of glucose	[195, 196]
Urease	Ag NPs, phosphonate grafted Fe_3O_4 NPs	Biosensors for urea in blood and urine, alcoholic beverages, natural water and environmental wastewaters	[197, 198]
Peroxidase	Au-chitosan NPs	Biosensor for H_2O_2 for water, pharmaceutical and biomedical applications	[199]
Glucose oxidase	Pt/FGS/chitosan, SiO_2 NP	Biosensor for glucose	[200–202]
Cyclodextrin glycosyl transferase, alcohol oxidase	Cellulose-Ag NPs	Biosensors for methanol and pectin methyl esters	[203–205]
Penicillinase	Ag NPs	Biosensor for penicillin	[62]
DNA ligase	Fe_3O_4	Biosensor for genomic DNA	[206]
Glucose oxidase	Au	Biosensor for glucose	[207–209]
DNA methyltransferase	Au	Electrochemiluminescence biosensor for DNA methyltransferase activity	[209]
DNA ligase	Au	Biosensor for genomic DNA	[206]
Esterase	Au	Biosensor for methyl parathion and malathion	[210]
Horseradish peroxidase	Au	Biosensors for cyanide	[211]
DNA methyltransferase	CdS	Electrochemiluminescence biosensor for DNA methyltransferase activity	[212]
Diamine oxidase	Pt	Biosensors for histamine	[213]

immobilization of lipases, and were applied for biofuel production [93–95].

Beyond laboratory benchtop, the development of industrial applications of NEs for biofuel production should take particularly care of costs related to the preparation of the nano-biocatalysts. At the same time, it is important to consider the possible negative impacts of nanomaterials for environment and health.

NEs for biomedical applications

Theoretically, enzymes can be used to treat a number of heart, oncological, viral and hereditary diseases [96–99]. Nevertheless, due to their short lifetime, rapid inactivation in the human body, and systemic immune reaction risks, enzymes' daily clinical use is not as widespread as it could [96]. Indeed, upon introducing a nanomaterial into a biological fluid, a protein shell is deposited, called protein corona, which can be hardly controlled. Notably, this protein corona is considered responsible for the awakening of the immune system and for the clearance of the nanomaterials from the organism. However, enzymes of interest bound to nanomaterials could be specifically distributed to the target location to tackle the above-mentioned drawbacks. Thus, the targeted delivery of NPs can possibly control the ratio between bound enzyme and nanocarrier for minimizing immunogenicity [100]. Although many NEs with considerable therapeutic potential looked promising in vitro and in studies using animals, they are not yet in the initial phases of clinical trials [100]. Nevertheless, several nanomaterials can count on a remarkable number of in vitro studies dealing with cell uptake, cytotoxicity, drug delivery and, most importantly, providing valuable hints on the correlation among nanomaterial nature and cell response.

Recent applications of NEs for biomedicine are reported in Table 3. Among the numerous biomedical applications of NEs, three areas were selected for a deeper insight, namely thrombolytic, anti-inflammatory and anti-bacterial therapies.

NEs for thrombolytic therapy

In order to prevent blood coagulation from acute myocardial infarction or cerebral micro-thrombosis, some enzymes, including tissue plasminogen activator (tPA), streptokinase and urokinase-type plasminogen activator (uPA), are

Table 2 Examples of enzymes immobilized on nanomaterials and applied for biofuel production along with their operating conditions, efficiency and stability

Enzyme source	Nano material	Substrate	Reaction temperature (°C)	Conversion efficiency (%)	Reusability (reaction cycles/operating days)	References
Burkholderia cepacia	Aminated magnetic NPs	Soybean oil	45	75	7	[214]
Burkholderia cepacia	Magnetic NPs	Soybean oil	40	88	10	[215]
Pseudomonas fluorescens	Co^{2+}- magnetic NPs	Cooking oil waste	50	83	10	[216]
Rhizopus oryzae	Magnetic NP modified graphene oxide	*Chlorella vulgaris* bio-oil	45	71	5	[217]
Rhizomucor miehei	Magnetic NPs modified multi-walled carbon nanotube	Cooking oil waste	50	94	10	[218]
Thermomyces lanuginosus	Magnetic NPs	Palm oil	50	97	5	[219]
Pseudomonas fluorescens	Magnetic NPs modified single-walled carbon nanotubes	Sunflower oil	–	99	20	[220]
Burkholderia cepacia	Magnetic NPs modified multi-walled carbon	Soybean oil	35	89	20	[221]
Candida antarctica	Fe_3O_4–SiO_2	Cooking oil waste	50	100	6	[222]
Burkholderia sp.	Fe_3O_4–SiO_2	Olive oil	40	90	10	[223]

currently employed in medical practice [100, 101]. MNPs, liposomes and polymeric NPs combined with the above-mentioned thrombolytic enzymes have been applied for their action at the blood clot site. The purpose was to eradicate the chance of unwanted heavy bleeding triggered by their non-targeted and non-specific activation [97]. Magnetic NPs were proposed as nanocarrier for targeted therapies to localize and concentrate thrombolytic proteins next to the coagulation site [98, 102–104]. Notably, properly engineered magnetic nanocarriers were applied for the effective supply of streptokinase to a canine carotid artery thrombosis along the external magnetic field [105]. As compared to non-mesoporous MNPs, mesoporous MNPs sensationally enhanced the thrombolytic activity. In addition, mesoporous MNPs are considered excellent candidate materials to enhance urokinase loading capacity up to 30-fold [101]. Likewise, to achieve ultrasound facilitated thrombolysis, tPA was immobilized using echogenic liposomes [106]. In another study, polystyrene latex NPs with a 40-nm size were used to covalently bind tPA and anti-fibrin antibodies. The covalently bound tPA and anti-fibrin antibodies were directly delivered at the coagulation location to lessen the possibility of systemic toxicity [107].

NEs for inflammation and treatment of oxidative stress

Reactive oxygen species (ROS) are unstable species, namely superoxide anion (O_2^-), hydrogen peroxide (H_2O_2) and hydroxyl radical (OH°), which can trigger oxidative stress and damages to cell structures [108]. ROS can be enzymatically and non-enzymatically produced by electron transfer reactions to molecular oxygen (O_2) in response to a number of conditions. ROS also damage various cell types, including epithelial cells, macrophages, neutrophils, eosinophils, monocytes, and lymphocytes [108–110]. Intense ROS generation occurs in innate immune cells at the inflammatory site. The phenomenon can be linked to chronic inflammatory diseases or external agents, such as microorganism infections or cigarette smoke in the lungs [109]. Furthermore, enzymatic sources of ROS, e.g., NADPH oxidases, present on the cell surface of active macrophages, produce superoxide anions [109, 110]. Cells are generally protected against endogenous ROS by the catalytic reactions which involve superoxide dismutase (SOD), catalase and peroxidases [111, 112]. In the case of excess ROS production, exogenous SOD and catalase can be provided at the inflammation site, even if the stability of these enzymes is relatively low. To shield catalase from proteolytic deprivation at the injection site, protease-impermeable nanocarriers, such as polyethylene glycol (PEG) and polylactic–polyglycolic acid (PLGA) copolymer-based substrate-permeable polymeric NPs along with oleate coated magnetite NPs, have been used. The enclosed catalase or peroxidase-based polymeric NPs were demonstrated to protect cell cultures against vascular oxidative stress [112]. For instance, polymeric NPs loaded with catalase or SOD achieved the pulmonary vasculature at 33% of intravenous injected dose in 30 min. Moreover, they

Table 3 Examples of enzymes immobilized on nanomaterials for biomedical applications

Enzyme	Nanomaterial	Application	References
Tissue plasminogen activator	Polystyrene latex NPs	Reduce the risk of systemic toxicity during thrombolytic treatment	[107]
Urokinase-type plasminogen activator	Magnetic NPs	Enhanced thrombolysis rate in a microfluidic channel	[224]
Tissue plasminogen activator, streptokinase	Cu NPs	Restores blood flow in arterial thrombosis	[225]
Urokinase-type plasminogen activator	Magnetic polyelectrolyte-based composites	Thrombolytic and anticoagulant properties	[226]
Tissue plasminogen activator	Magnetic iron oxide micro-rods	Enhanced thrombolysis after ischemic stroke	[227]
Catalase, SOD	Polymeric NPs	Protection against inflammation	[111]
Catalase, peroxidase xanthine oxidase	Polyethylene glycol and poly-lactic/polyglycolic acid nanocarriers	Protection and vascular oxidative stress	[228]
SOD	Poly(lactide-co-glycolide), polybutylcyanoacrylate, liposomes	Protection against reperfusion injury	[229]
Catalase	Poly(lactic *co*-glycolic acid) NPs	Protection of neurons from oxidative damage	[230]
Catalase, SOD and glutathione peroxidase	$Cu_{5.4}O$ NPs	Cytoprotective effects against ROS-mediated damage	[231]
Lysozyme	Silver NPs	Antibacterial activity against various resistant bacterial strains	[119]
lysozyme	NPs functionalized with pathogen-specific antibodies	Enhanced antimicrobial activity against *Listeria monocytogenes*	[118]
Lysozyme	Chitosan NPs	Enhanced antimicrobial activity against various bacterial strains	[232]
Catalase	Mouse anti-human (ICAM-1) nanoparticles	Protection of endothelial cells from oxidative stress	[233]
Lysozyme	Selenium NPs	Synergistic antibacterial properties	[234]
Streptokinase	Alumina nanoparticles	Thrombolytic colloid with prolonged action	[235]
Tissue plasminogen activator, streptokinase	Chitosan nanoparticles	Treatment of thrombolytic disorder	[236]
	Polyethylene glycol, poly(lactic-co-glycolic acid, NPs	Enhanced thrombolytic activity	[237]
Urokinase	Chitosan nanoparticles	Enhanced thrombolytic activity	[238]

safeguard mice from the endotoxin-induced acute inflammatory effects in the lungs [111]. It should be mentioned that the prolonged use of PEGylated materials may result in the development of anti-PEG antibodies and in the phenomenon described as "accelerated blood clearance" (ABC).

SOD, delivered by NPs specifically to the site, has been investigated as an anti-apoptotic and anti-inflammatory substance in the central nervous system (CNS). SOD-based poly-butyl cyanoacrylate (PBCA) NPs could pierce across the blood–brain barrier with ease. SOD bearing NPs also targeted the enzyme to the CNS while retaining most of the enzymatic functionality and receptor-binding capability [113–116]. Lately, mesoporous silica NPs loaded with the enzyme fused with a cell-penetrating peptide, which arises out of the human immunodeficiency virus 1 (HIV-1) transactivator of transcription protein [117], have been applied for an effective intracellular SOD delivery.

NEs for antibacterial treatment

There is a plethora of literature available on the use of enzyme-conjugated NPs against several human microorganisms, such as *M. tuberculosis*, *E. faecium*, *S. aureus*, and *P. aeruginosa* [118–120]. Most reports deals with the application of lysozyme from hen egg white. Lysozyme, also referred to *N*-acetylmuramic hydrolase, is a monomeric protein stabilized by disulfide bridges of its polypeptide chain, able to cleave β-(1,4)-glycosidic bonds between *N*-acetylmuramic acid and *N*-acetylglucosamine of bacterial cell wall, showing high antimicrobial efficiency against gram-positive bacteria. In this view, lysozyme was coupled

to polystyrene (PS) NPs against *Listeria monocytogenes*. The enzyme was co-immobilized with an anti-*L. monocytogenes* antibody onto PS-NPs, and presented a higher catalytic activity than both native lysozyme and antibody-free lysozyme-modified NPs [118]. Specifically, lysozyme immobilized on immune-nanoparticles at 35 µg/mL final concentration reduced *L. monocytogenes* from 5 log CFU/mL to below the detection limit (< 1 log CFU/mL) in 3 h. Differently, when lysozyme (500 µg/mL) was used, 2 log CFU/mL *L. monocytogenes* cells remained after 5 h treatment. Furthermore, AgNPs with notable antimicrobial potential have been verified as an effective agent against various silver ion resistant bacterial strains with the assistance of lysozyme [119].

NEs for biotechnological applications

Lately, molecular biotechnology and nanoscale science development showed many improvements, which revealed the fine-tuning of protein structures, the management of enzyme nano-environments and the properties of nanomaterials [6]. In comparison to macroscopic carrier supported immobilized-enzymes, a nano-biocatalyst can accomplish a higher enzyme loading due to the very high surface to volume ratio, often reaching several tens of m^2 of available space for enzymes binding per gram of nanomaterial, and meaningfully improved mass-transfer efficiency regarding the accessibility of the substrates to the immobilized enzyme [121]. Indeed, nano-biocatalysis development led to the improvement of different biotechnological processes and two examples are hereafter reported.

NEs for proteomic analysis

Proteomic studies based on the development of mass spectrometry have received amplified consideration in the past several years, mainly because the major proteins involved in different biochemical and signaling pathways can be elucidated. Moreover, this approach significantly contributed to the advances of highly effective drug formulations [122]. The digestion of proteins in the sample is obtained by trypsin, and represents a fundamental step of proteome analysis by mass spectrometry, mainly because of the enzyme high specificity, widespread availability and ease of use. In this context, a nano-reactor constituted of nanoporous silica has been utilized as trypsin carrier to digest proteins. The proposed system accelerated the sample preparation procedure and produced superior trypsin digestion outcomes compared to conventional bulk processes [2, 3, 123–125]. In this case, nanoporous silica was used to bind the target protein molecules by simple absorption, and then the protein bearing nanomaterial was incubated in a trypsin solution. The 'in-nanopore' protein hydrolysis method improved trypsin digestion, allowing a more efficient peptide production, a drastic reduction of working time and an optimized mass spectrometry analysis. Alternatively, proteases immobilized on nanosized solid supports have gained popularity because of the limited volumes employed, which allow to obtain high enzyme concentrations. This results in a short digestion time, low probability of autolysis and the reusing of bound enzymes [126–129]. A number of nanomaterials, such as graphene oxide (GO) [130–132], hybrid aerogels [133], magnetic NPs [134–136], nanotubes [137, 138] and porous reactors [139, 140] have been proposed to immobilize digestive enzymes leading to improved results with respect to soluble enzymes.

NEs for antifouling applications

Almost any material, upon introduction in biological systems, undergoes the nonspecific binding of macromolecules, mainly proteins, which completely coat its surface. In the presence of microorganisms, the phenomenon is called "biofouling" and leads to microbial cell accumulation on the material surface, signifying an obstacle for implants, biosensors, and other hospital equipment [9]. A lot of work has been dedicated to the development of antifouling membranes to efficiently avoid or lessen biofouling complications. An ecological method is represented by the combination of enzymes with antifouling paints. For instance, new antifouling paints were created with different proteases, and tested as active antifouling agents to lessen surface protein binding. They were able to prevent the formation of protein-based glues, and thus deter microorganisms from binding onto surfaces [141–143]. Nano-bio-catalytic systems have proven their efficacy for reducing protein binding onto surfaces due to the effects of nanomaterials on improving enzyme stability. As compared to native enzymes, SWNT-protease conjugates exhibited a higher enzyme stability [144]. Moreover, SWNT-protease conjugates also proved to be active as self-cleaning nano-bio-composite films [145]. Operationally stable nano-bio-catalytic systems with antifouling and self-cleaning features are expected to subsidize the expansion of long-lasting antifouling coatings. Such effective antifouling can deter or postpone microbes from adhering to surfaces of medical implants, and of analytical devices, such as biosensors, which can stand the presence of microorganisms for long time.

NEs for wastewater treatments and environmental decontaminations

Common sources of dyes and/or colorants, namely effluents or sewage water from diverse manufacturing plants, including textiles, papermaking, tannery, and printing, are considered carcinogenic and dangerous even at low concentrations. These effluents can be remedied by using enzymes, including laccases, peroxidases, or lipases for lipid wastes [86, 146, 147].

Harsh physical and chemical conditions, often encountered in effluent streams, might lead to modifications of the native enzyme conformation, thus altering enzyme functionality with the concomitant loss of catalytic activity. Immobilization on solid supports minimizes the loss of enzyme activity under operating conditions, also allowing the biological component to be reused. As an example, horseradish peroxidase (HRP) immobilized onto magnetic NPs preserved high catalytic properties and durability, performing efficient decolorization of azo-dyes [148]. Likewise, recalcitrant contaminants in wastewater were treated using oxidative enzymes, such as laccases, immobilized on carbon nanotubes [149].

Examples of applications of nano-enzymes for wastewater treatment are reported in Table 4.

The use of enzymes immobilized on NPs for wastewater treatment is of particular interest for encompassing the degradation of pollutants to less-harmful by-products [150]. The remediation of polluted wastewater can be accomplished by combining experiences on protein chemistry and biochemistry and nanotechnology for the development of single enzyme NPs, SENs [151]. In the case of environmental applications, particular care should be devoted at guaranteeing the proper enzyme stability of the NE under possible harsh conditions. As an example, SENs can be produced by using a porous silicate shell encapsulating the enzyme molecule, which remains accessible to substrates. SEN preparation aimed at degrading recalcitrant compounds, such as phenols, poly-aromatic dyes and pesticides, can be conducted by using cell-free unrefined extracts or purified enzymes, such as peroxidases, polyphenol oxidases, dehalogenases and hydrolases [151]. Moreover, NEs were widely used for drinking water purification because of their low toxicity and high biodegradability [152].

The use of NEs for the textile and detergent industries

Fabric manufacturing is gaining a reputation for substituting commonly utilized toxic chemicals with ecological-friendly biomolecules [153]. Thus, many textile industry businesses developed methods involving enzymes for catalysis rather than harmful and polluting substances, such as formaldehyde, chlorine and heavy metals [154]. The most used enzymes in fabric manufacturing are cellulases, amylases, pectin lyases, catalase, laccases, and peroxidases, which have been extensively applied for the last stage of denim production, cotton softening, scrubbing, bleaching and/or bleach termination, and excess dye removal [155]. Among these enzymes, cellulases were introduced first and are still used in a large amount. As operating conditions in industrial plants involve high temperatures and extreme pH values, enzyme denaturation could quickly occur. In order to avoid this drawback, enzyme immobilization is often applied. As an example, the covalent immobilization of cellulase on poly-methyl-methacrylate maintained enzyme activity for several process cycles [86, 156, 157].

The enzymes belonging to the class of alkaline proteases are the most widely utilized in the detergent business. They are generally extra-cellular product of several bacterial strains and are characterized by excellent catalytic properties and durability under heat stress, alkaline pH values and in the presence of oxidizing agents [158]. These enzymes demonstrate good proteolytic activity and high stability due to the high degree of hydrogen bonds, disulphide bridges and hydrophobic interactions.

Alternatively, amylases, lipases, and cellulases are also commonly utilized in the detergent industry for textile cleaning [159–161]. An example of the industrial use of NEs is α-amylase immobilized on silica NPs, leading to increased activity and stability, thus improving cleaning efficiency towards starch in laundry detergents [162]. Examples of NEs applied in fabric, detergents and tannery manufacturing are reported in Table 5.

Applications of NEs for food industry

Food processing commonly utilizes immobilized enzyme to improve production processes. Indeed, biocatalysts can operate on a specific substrate, leaving all the other food components unmodified, at solvent, pH and temperature conditions compatible with the preservation of food organoleptic properties. Moreover, immobilized enzymes can be used in continuous processing techniques, allowing the reuse of catalysts until their denaturation. The possibility to automate the process and consequently save time represents another favorable aspect of immobilized enzymes. Regarding enzymes immobilized on nanomaterials, baking, dairy production, beverage processing and starch conversion are the most important areas of application (Table 6). In particular, examples of applications and the role of nano-enzymes in different food industries are below reported.

Table 4 Examples of enzymes immobilized on nanomaterials for waste treatment and water decontamination

Enzyme	Nanomaterial	Application	References
Laccase	Multi-walled carbon nanotubes	Removal of bisphenol A from water	[239]
Laccase	Cu(II)-chelated chitosan nanoparticles	Degradation of phenolic compounds	[240]
Horseradish peroxidase	Fe_3O_4/nanotubes	Removal of phenols from wastewater	[241]
Laccase	Inorganic hybrid nanoflowers	Bisphenol A degradation in water	[242]
Laccase, peroxidase, dioxygenase	Chitosan-magnetite nanoparticles	Degradation of cibacron redazo dye	[243]
Laccases	Titania nanoparticles	Biotransformation of pollutants such as diclofenac and acetaminophen in groundwater	[244]
Horseradish peroxidase	Nanogel	Removal of phenolic compounds from wastewater	[245]
Laccases	Mesoporous carbon nanospheres	Removal of antibiotic contaminants	[246]
Horseradish peroxidase	Graphene oxide nanopowder	Adsorption of methylene blue from aqueous solutions	[247]
Laccase	Polyamide 6 nanofibers	Biodegradation of endocrine disrupting chemicals, such as triclosan, bisphenol A, and 17α-ethinylestradiol	[248]
Horseradish peroxidase	Graphene oxide Fe_3O_4/Au@citric acid nanoparticles,	4-Chlorophenols removal from wastewater	[249]
Horseradish peroxidase	Fe_3O/nanodiamond nanocomposites	Phenol degradation	[250]
Laccase	Polyamide6/chitosan nanofiber	Removal of bisphenol A and α-ethinylestradiol	[251]
Laccase	Chitosan-functionalized supermagnetic halloysite nanotubes	Degradation of Direct Red 80	[252]
Laccase	Metal oxides nanomaterials	Degradation of alizarin red S dye	[253]

NEs for beverage industry

Glycosidases, which hydrolyze glycosidic linkages, can release volatile substances and aromatic scents, and thus improve aroma and fragrance of drinks, including alcoholic beverages and liquids obtained from fermentation products of fruits [163]. As an example, β-glucosidase immobilized on chitosan modified multi-walled carbon nanotubes (MWCNTs) by covalent binding led to a significant increase of aroma compounds in tea. For example, the most important tea aroma components such as benzyl alcohol, geraniol, nerol, linalool and 2-phenylethanol increase by 160%, 68.72%, 67.68%, 17.93% and 4.15% in treated green tea, respectively. At the same time, immobilization modified the optimum temperature of the enzyme from 35 to 45 °C and improved its storage stability: immobilized β-glucosidase still retained 72% of its original catalytic properties after reusing 10 times [164]. Moreover, β-glucosidase immobilized on SiO_2 NPs significantly increased the amount of polyphenols in sugar cane juice samples [225].

Table 5 Examples of enzymes immobilized on nanomaterials and applied in textile, detergents and tannery manufacturing

Enzyme	Nanomaterial	Application	References
Lipase	ZnO nanoparticles	Applied for removal of oil and grease stains from cotton fibers	[254]
Cellulose	Nanospheres	Stains removal from textiles	[255]
α-Amylase	Silica nanoparticles	Enhanced cleaning efficiency toward starch removal on cotton fabrics	[162]
Protease	Silica nanoparticles	Showed increased cleaning efficiency toward protein soil removal on cotton fibers	[256]
Cellulose	ZnO/cellulose nanocrystals	Absorption of cationic dyes	[257]
Metallo-protease	Nano-hydroxyapatite	Removal of blood stains from textiles	[258]
Protease	Mesoporous silica nanospheres	Used for laundry detergent formulations	[259]
Manganese peroxidase	Iron oxide/chitosan nanocomposite	Discoloration of textile wastewater	[260]
Catalase	Fe_3O_4 NPs	Decomposition of hydrogen peroxide	[261]

NEs for fruit juice industry

The application of nanotechnology, by using nanoencapsulation and nano-emulsions, to beverages was proposed to provide new methods to improve safety and nutritional value of products, including a possible reduction of the use of preservatives, salt, fat and surfactants.

In the processing of fruit juices, an important complication is represented by the presence of polysaccharide components, such as pectins, in the form of disrupted fruit cell walls. Pectins are constituted of D-galacturonic acid monomers, connected by α-1,4-glycosidic linkages [165]. Pectinolytic proteins could be found in plants, bacteria, fungi, and yeasts, and are able to hydrolyze α-1,4 glycosidic linkages involving D-galacturonic acid monomers [166]. In the food industry, basic pectinases are used for retting fruit materials, while acidic pectinases are widely used for the precipitation macroscopic materials, for improving extraction and fining of juices from vegetables and fruits [167]. Pectinases immobilized on chitosan modified magnetic NPs, using dextran polyaldehyde as a macromolecular cross-linker, were applied to reduce the turbidity of apple juice [168]. For the clarification of pomegranade juice, the immobilization of a protease from *Penaeus vannamei* on chitosan NPs was studied and compared with the soluble enzyme [24]. *P. vannamei* protease immobilized on chitosan nanoparticles retained an activity of 100% at 70 °C for 1 h, whereas the activity of the soluble enzyme was only 17% under the same conditions. At the same time, the catalytic parameters of the biocatalyst resulted practically unmodified upon immobilization.

Xylanase immobilized on 1,3,5-triazine-functionalized silica-based magnetic NPs were proposed to aid xylan removal [169]. It should be noted that glycosidases, often present as impurity in commercial pectinases, cause the reduction of juice color due to their action on anthocyanins [170].

NEs in milk processing

Milk represents a significant part of the human diet in the entire world since ancient times. Lactose, β-D-galactopyranosyl-(1 → 4)-D-glucose, is the second component in milk, comprising about 4.8–5.2%. After intake, lactose is commonly hydrolyzed into galactose and glucose, which are absorbed by the small intestine. However, the lack of adequate amount of lactase (β-D-galactosidase) in the gastrointestinal tract is commonly found in non-Caucasians, aged people of Western countries, and in several ethnic population groups, leading to lactose intolerance. Immobilized lactase (β-galactosidase) converts lactose into glucose and galactose, and was proposed in milk processing. Indeed, in order to favor lactase-deficient people, lactose-free milk

Table 6 Examples of enzymes immobilized on nanomaterials for applications in food industry

Enzyme	Support material	Application	References
α-Amylase	Cellulose-coated MNPs	Starch hydrolysis	[262]
α-Amylase	TiO_2NPs	Starch hydrolysis	[263, 264]
GOx	Thiolated Au NP	Determination of glucose	[265, 266]
β-Galactosidase	Con A layered ZnO NPs	Lactose hydrolysis	[267]
Diastase	Nickel NPs	Starch hydrolysis	[268]
α-Amylase	Au nanorods	Starch hydrolysis	[19]
Diastase α-amylase	AgNPs-doped gum acacia–gelatin–silica nanohybrid	Starch hydrolysis	[269]
α-Galactosidase	Graphene nanosheets	Hydrolysis of raffinose oligosaccharides	[270]
β-Glucosidase	SiO_2 NPs	Sugarcane juice treatment to increase phenolics	[271]
β-Galactosidase	ZnO NPs	Lactose hydrolysis	[272]
β-Galactosidase	Fe_3O_4-chitosan NPs	Galactooligosaccharides production	[272]
β-Galactosidase	MWCNTs	Lactose hydrolysis	[273]
β-Galactosidase	Polysiloxane polyvinyl alcohol magnetic composite	Lactose hydrolysis	[274]
β-Galactosidase	MNPs	Galactooligosaccharides production	[275]
β-Galactosidase	Nanodiamonds	Lactose hydrolysis	[276]
β-Galactosidase	Ag NPs	Lactose hydrolysis	[277]
β-Galactosidase	Polyaniline–chitosan–Ag-	Lactose hydrolysis	[278]
β-Galactosidase	Fe_3O_4@PANI-GO	Lactose hydrolysis	[279]
Lipase	Nano-cellulose/polypyrrole/GO	Synthesis of flavors	[280]
Alcohol dehydrogenase	Au and Ag NPs	Alcohol synthesis	[281]
Trypsin	Ag-PDA-NC	Protein hydrolysis	[282]
Raffinase	Fe_3O_4 NPs	Galactose and sucrose production	[283]

is commonly produced by a continuous process in a flow reactor containing immobilized lactases. Alternatively, the enzyme can be immobilized on nanomaterials: Lactase (*Aspergillus oryzae*) was covalently bound to magnetic NPs by carbodiimide crosslinker chemistry. The enzyme–NP conjugate showed a similar catalytic activity compared to the native enzyme [171], and, in comparison with the soluble enzyme, the immobilized lactase can be recovered for repeated use with limited loss of enzymatic activity (78% activity retention after 5 operative cycles).

NEs in soluble carbohydrate and starch manufacturing

α-Amylases hydrolyze endo-α-1,4-glycosidic bonds of starch producing smaller molecules, including glucose, maltose and other oligomers. Amylases are essential biocatalysts in biotechnology, representing about 25% of the entire enzyme business of the food industry. α-Amylases are primarily found in plants, animals, and microbes [172–174]. They are heavily used for the enzymatic hydrolysis of starch to obtain glucose-rich solutions. These solutions are then converted to high fructose syrup (HFS), which is an ideal substitute for sucrose as sweetener, as fructose is 30% sweeter than sucrose and is more soluble in water compared to glucose. α-Amylases were immobilized by adsorption on the surface of ZnO and Fe_3O_4 nanoparticles for the optimized hydrolysis of starch [175].

Glucose isomerase catalyzes the conversion of glucose to fructose, and the final syrup contains 42% w/w fructose. Glucose isomerase was immobilized on iron oxide loaded mesoporous silica NPs, along with cellulase, for a constant high yield of fructose production [175]. The proposed system was applied for the optimized multistep conversion of cellulose-to-glucose-to-fructose in continuous, with a constant yield (51%) comparable to the maximum obtained in food industry.

Alternatively, HFS can be produced from solutions obtained from the extraction of sucrose-producing plants by the enzyme invertase [176].

NEs in meat industry

The growing demand for sustainable meat production led industries to focus on the innovation of the production and treatment of processed meat. New functional properties were proposed for processed meats and packaging adopting nanotechnology, with the potential to influence the meat processing business [177]. The main advantages of utilizing nanomaterials in meat are improved bioavailability of bioactive compounds, antimicrobial effects for enhancing shelf-life and increased sensory acceptance.

The determination of meat quality can be obtained by nano-based biosensors for the evaluation of degradation products of ATP, namely hypoxanthine. As an example, a graphene-titanium dioxide (TiO_2-G) nanocomposite was applied as support for the immobilization of xanthine oxidase, which catalyzes the oxidation of hypoxanthine [178]. Alternatively, meat quality can be assessed by determining the concentration of biogenic amines, such as histamine, tyramine, putrescine and cadaverine [179]. As an example, tyrosinase was immobilized on functionalized carbon nanotubes for the determination of tyramine in fish meat [180].

However, for the direct application on food products, doubts on public acceptance, costs and regulation regarding the introduction of nanomaterials in meat processing are still to present and should be addressed.

NEs for food waste treatment

The application of nano-bio-catalysis systems on food wastes for extracting specific natural substances has the double advantage of reducing waste quantities and increasing economic resources of the agri-food sector [181]. The application of cellulolytic enzymes on natural waste sources, such as peels, skins and husks of various fruit and vegetables, releases several biological compounds, including colored compounds, polyphenols, minerals, and other bioactive substances [182, 183]. Cellulases have been immobilized onto MnO_2 NPs with improved activity and applied to break up agricultural wastes for obtaining valuable products [184]. Glutaraldehyde chemistry was used to co-immobilize pectinase and cellulase onto magnetic NPs through their amino groups. These enzymes were utilized to isolate antioxidants and to improve the solvent extraction of carotenoid compounds from peels of oranges [185]. Further, magnetic NP-immobilized enzymes were reused after many isolation processes [186]. The synthesis of galacto-oligosaccharides, lactulose and lactosucrose, lactose has been conducted with magnetic NP-immobilized β-galactosidase [187]. These galacto-oligosaccharides are important components in the food processing business and need to be constantly produced. Therefore the nano-bio-catalysis-mediated approach mentioned above has been broadened [188].

Concluding remarks and perspectives

Born as a fusion of nanotechnology and enzyme chemistry, nano-bio-catalysis has achieved tremendous progress, which revealed advantageous for industrial applications. Enzyme immobilization on nanomaterials has made impressive advances in enzyme stabilization and reusability. Nonetheless, the large-scale application of nano-bio-catalytic systems has several obstacles, such as the complexity of

nanomaterial synthesis and the need, in the vast majority of cases, of proper coating modifications of the nanosized supports for enzyme immobilization. Surface modification of nanomaterials in order to stand the different operating conditions, such as long-term colloidal stability and specific surface chemistry, is usually necessary. Unfortunately, in many cases the synthesis of nanomaterials involves the use of organic solvents or toxic substances, which could associate the production of nanoparticles with environmental impacts. Notably, often immobilization leads to enzyme inactivation and to the loss of catalytic properties. Thus, both the nanomaterial and the enzyme for NE preparation should be properly selected, as well as attention should be paid to optimize the immobilization procedure and conditions. Nowadays, a huge amount of different nanomaterials is available, each one characterized by specific properties and costs. At the same time, enzymes belonging to a wide variety of classes and produced by different biological sources are available. As a consequence, their catalytic behavior and structural stability may be very different. Anyway, the possibility to reduce the amount of enzyme, representing by far the most costly component of the nano-bio-catalyst, worths the efforts due to implement these systems in industrial processes. Still, for the ultimate and complete introduction of nano-bio-catalytic systems at industrial level, several aspects of the interactions between enzymes and nanomaterials need to be further elucidated.

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Declarations

Conflict of interest Authors declare that there is no conflict of interest regarding the publication of this paper.

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