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TUTORIAL REVIEW

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Nanotechnology for sustainable food production: promising opportunities and scientific challenges

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The agro-ecosystem is under enormous pressure due to rapid population growth, increasing global food demand, increasing fresh water withdrawals and energy consumption, excessive food waste, inefficient use of agrochemicals, environmental degradation and climate change. Nanotechnology offers opportunities to make food production more sustainable by providing better sensors for monitoring physical, chemical, or biological properties and processes; technologies for controlling pathogens to increase food safety and minimize food waste; improved membranes and sorbents for distributed water treatment and resource recovery; novel materials for timed and targeted delivery of agrochemicals; and, new materials for monitoring and improving animal health. This tutorial review provides an overview of the nanotechnology opportunities of greatest potential determined through an NSF-funded interdisciplinary workshop of ~50 experts from the U.S. and the EU in the areas of nanotechnology, energy, water, agriculture, systems engineering, data integration and analysis, and social science. This paper also presents examples of selected specific opportunities and the remaining scientific and engineering challenges that must be overcome to realize the benefits of nanotechnology across the farm to fork continuum.

Environmental significance

Currently, global agri-food production is highly inefficient due in part to poor utilization efficiency of fertilizers and biocides and food waste. This in turn causes significant environmental collateral damage, expected to be aggravated further with increasing populations and global food demand. Specific nanoscale properties of nanomaterials allow unique and favourable interactions with natural and built systems that can be leveraged to the increase efficiency of sensor platforms, pathogen control strategies, water treatment, resource recovery, agrochemicals, and animal heath surveillance and control, thus making agri-food systems more sustainable. This tutorial review discusses promising opportunities and scientific challenges for nanotechnology to promote efficiency of food production.

Introduction and objectives

In 2050, the global population is projected to be ~9.6 billion and associated global food demand is expected to increase by 70% to 100%.[1–3] Agriculture accounts for a large fraction of energy and water use. Globally, between 6% (ref. 4) and 30% (ref. 5) of total energy use is consumed in the agri-food chain, producing 20% of greenhouse gas emissions. Over 70% of global water use is currently used for food production[3] and this is projected to increase to over 83% by 2050 to meet the growing food demand.[4] Agrochemicals use is notoriously inefficient. Globally, a large fraction of the 2.5 million tons of pesticides applied per year are either lost to the air and run-off or unable to effectively reach target.[6–8] Estimates

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suggest that 30–50% of pesticide losses occur to the atmosphere during spray application.[9] Similarly, between 50 and 70% of total applied nitrogen is lost.[10,11] Inefficiencies in food production are compounded further by food waste. Between 1.3 and 2 billion tons of food produced annually (around 33% to 50% of global food production) spoils due to microbial contamination or package expiration and is wasted in the supply chain.[12] The current scenario of intensive irrigation and inefficient use of fertilizers, biocides, and processed food is stressing ecosystems and natural resources, and causing significant environmental collateral damage, including increasing soil erosion rates, degradation of land and soil conditions, soil pollution, biodiversity loss, increasing water withdrawals, degradation of water quality, disruption of global nutrient cycles, and increasing energy consumption and greenhouse gas emissions.[1]

The loss of livestock to disease also represents a significant loss of water and energy investment as well as capital. Animal diseases such as zoonoses (*e.g.* mad cow disease, avian influenza, H1N1 influenza, Nipah virus, among others) represent around 17% of annual animal production costs in industrialized countries and more than 34% in developing countries.[13] The efficiency of livestock operations in several areas of the world is also hampered by low fertility and challenges in animal reproduction.[14]

Food, energy, and water security are inextricably linked in agri-food systems. For example, electricity powers groundwater pumping for irrigation in certain areas (often semi-arid places). Inefficient use of fertilizers represents large energy losses given that production processes of nitrogen based fertilizers (*e.g.* with natural gas) are highly energy-intensive.[15] Wasted food also includes the loss of embodied energy and water. When basic sustainability principles are met, nanotechnology and nanomaterials can help to reduce the overall inputs of energy and water for food production, lower the overall ecological footprint of agriculture and associated collateral environmental damage, and offer better management of animal health (Fig. 1). However, there are a number of scientific and engineering challenges that must be overcome to realize these opportunities.

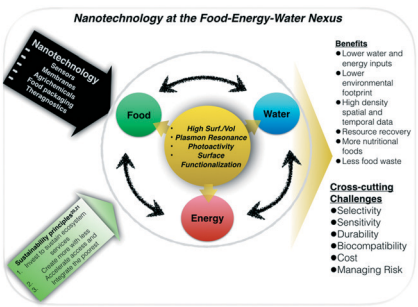

Fig. 1 Potential system-level benefits for nano-enabled technologies that are provided by the novel properties of engineered nanomaterials, and the major cross-cutting challenges that must be addressed to allow nano-enabled technologies to improve sustainability at the FEW nexus.[5,16,17]

Although opportunities for nanotechnology to improve agri-food systems are generally less well explored than applications for energy[18–20] or water treatment,[21–23] there are indications that the large surface to volume ratios, unique surface functionalization properties, plasmon resonance, and photoactivity of nanomaterials can be leveraged to make agri-food systems more efficient. This can occur by (1) providing a large surface area to enhance molecular adsorption and other surface reactions, (2) generating optical, electronic or electrochemical effects to improve sensitive detection, (3) providing highly porous and surface functionalized materials for timed and targeted release of agrochemicals, or (4) enabling unique photocatalytic and redox activity to improve antimicrobial activity. For example, nanosensors can enable the highly sensitive detection of moisture, pH, pathogens, pesticide residues or toxins in soil, water, air, plants tissues or food, as well as provide data on soil quality, crop performance, disease surveillance or food spoilage/safety at high spatial and temporal resolution. Nanotechnology can minimize food loss and waste through advanced food packaging and nano-based systems for antimicrobial disinfection. Opportunities exist to develop multifunctional delivery platforms for agrochemicals that provide targeted delivery, with the ultimate goal of achieving near-atom use efficiency. Similar capabilities exist for veterinary medicines and animal vaccines, increasing efficiency and minimizing excretion of drugs to the waste stream and the environment. Nanotechnology may also improve adsorption, fouling, photocatalysis, as well as membrane and magnetic separation processes thus enabling selectivity and greater efficiency in the recovery of nutrients and energy, removal of pesticides and contaminants and water treatment.

This tutorial review presents promising opportunities identified at an NSF-sponsored FEW workshop,[24] and identifies the key scientific, engineering, and social challenges to implementing those technologies and realizing the promised systems-level benefits. There are a number of critical scientific challenges that cross-cut many of the proposed applications such as improving selectivity, sensitivity, durability, biodegradability, and enabling performance in complex matrices with many potential interferences. Such engineering challenges are similar for sensors, a membrane for water treatment, or a new vaccine. These challenges are discussed in more detail for the proposed high value opportunities presented in this tutorial review. Continuing research efforts should be directed towards closing the knowledge gaps identified in the workshop.

Promising opportunities for nanotechnology to improve sustainability of agri-food systems

Promising opportunities identified for nano-enabled technologies to improve sustainability of agri-food systems include the following:

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• Sensors for monitoring chemicals, for assessing physical, chemical, or biological properties and processes, and for detecting pathogens or toxins.

• Technologies for controlling pathogens to increase food safety and minimize food waste.

• Membrane and sorbent technologies for distributed water treatment and resource recovery.

• Materials for timed and targeted delivery of agrochemicals.

• Materials for monitoring and improving animal health.

Fig. 2 summarizes the nanoscale properties that can be leveraged in these applications, and the anticipated benefits. In the following sections the rationale for selecting each of these high value opportunities is described, followed by specific examples of opportunities that leverage these nanoscale properties to improve performance and the underlying mechanisms of action. The current status of technology development and the key scientific, engineering, and social challenges to implementing these approaches and realizing their benefits are summarized.

Nano-enabled sensors and probes for environmental and food monitoring and pathogen detection

Nano-enabled sensors and probes hold tremendous potential to improve agricultural productivity per unit water, energy, or agrochemical input by providing highly distributed, real-time sensing of key performance metrics for crops and livestock at high spatial and temporal resolution needed for precision agriculture approaches.[25,26] Here we distinguish nano-enabled sensors from nanoprobes. Nanosensors measure an analyte concentration and require rapid and reversible binding, *i.e.* if the concentration goes down the signal goes down. Nanoprobes are devices that can selectively detect the presence of microbes or specific chemicals, requiring high sensitivity but is not necessarily reversible or quantitative. Each has a different principle of operation and therefore different challenges to development and implementation.

Nanosensors and nanoprobes have several benefits over traditional sensors. They generally leverage the unique optical and electrical properties of nanomaterials, high surface to volume ratio, and readily functionalizable surfaces are to measure and detect the presence of specific chemicals or pathogens in environmental or food samples with a higher level of accuracy and sensitivity than currently exists.[25,27] Nano-enabled sensing also can be performed with lower sample volumes due to their miniaturization capacity and lab-on-chip technology platforms.

Research and development of nanosensors for many agriculturally relevant analytes are ubiquitous in the literature. Analytes include pesticides, fertilizers, DNA and proteins in water and agri-food systems (*e.g.* nanosensors have been reported to measure DDT, 2,4-dichlorophenoxyacetic acid, carbofuran, triazophos, pyrethroid, methyl parathion, dimethoate or residues of organochlorines, organophosphates, and carbamates in water and/or vegetables).[7,25,26,28–39] Nanoprobes have been developed for the detection of small organic molecules, colorant additives and adulterants in foods, and nanosensors have been developed for the measurement of contaminants, glucose, antioxidants, flavour compounds

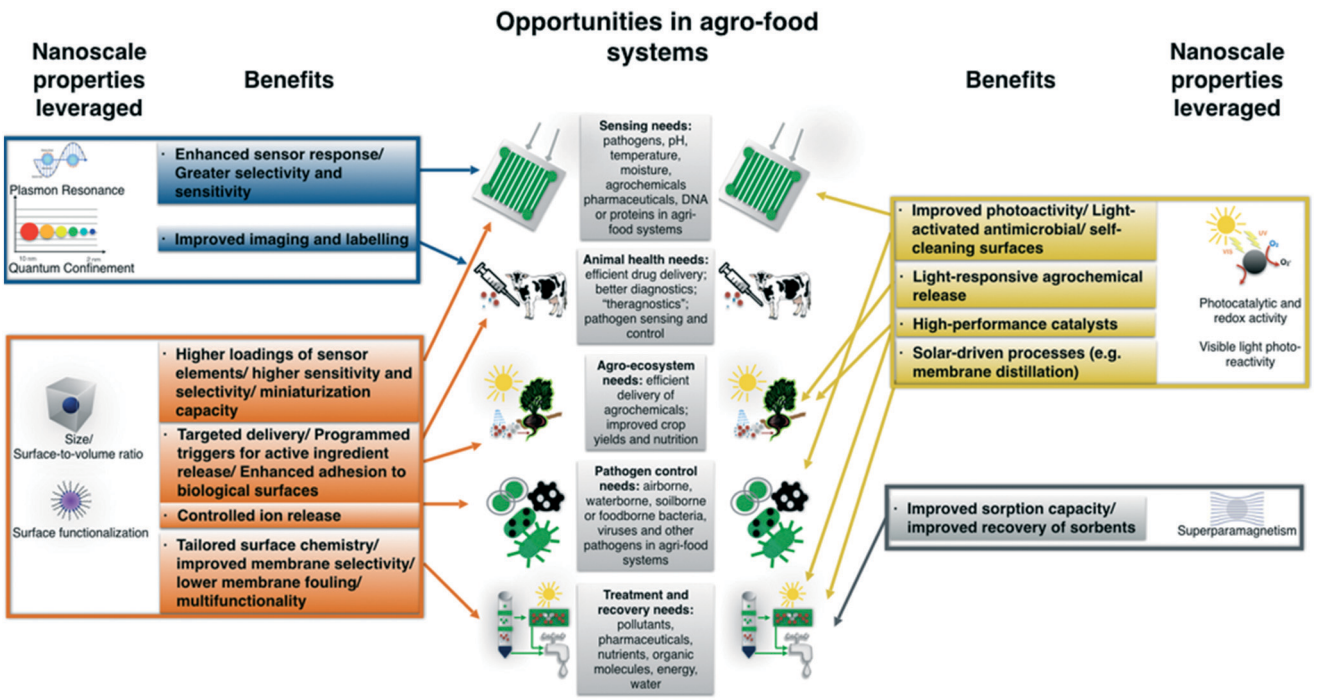

Fig. 2 Overview of the nanoscale properties leveraged, target opportunities, and the potential benefits of nanotechnology applications in agri-food systems. Analysis of the different opportunities indicates that the benefits resulting from the nanomaterial size and/or surface to volume ratio, surface functionalization, and photocatalytic activity are most often leveraged.

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and vitamin contents in foods.[40] Nanoprobes have also been developed for non-invasive gas sensing (*e.g.* to detect oxygen, carbon dioxide, gaseous amines or volatile organics associated with fruit spoilage) and for the detection of food-borne pathogens.[40]

Advances in sensor and probe technologies are anticipated to continue because nanomaterials offer a great variety of detection methods (*e.g.* electronic, colorimetric, fluorimetric or mass changes), and can be combined with microfluidic devices and cantilever arrays to develop multianalyte array sensors to further increase sensitivity and selectivity, enabling detection of target analytes (*e.g.* an antigen, target DNA, urea, glucose or a pesticide) at femtomolar level in some cases.[7,26,41] The unique optical and electrical properties associated with the high surface-to-volume ratio of nanomaterials allows increased surface loadings of biologically sensitized elements (*e.g.* enzymes, antibodies, lectins or nucleic acids) per mass of material and/or highly sensitive transducers (*e.g.* using conducting polymers which are functionalized with biological recognition elements) which provide greater selectivity and interface sensitivity compared to non-nanoscale analogs.[42,43] Nanomaterials can be used both as supports for immobilization of biomolecules and as labels for signal transduction and amplification.

Nanomaterials can also provide highly localized/sensitive detection of pathogens or toxins.[26,27,44] For example, nanoprobes for detecting single nucleotide changes of bacteria or viruses[45] or immunosensors to detect disease in wheat using surface plasmon resonance have been proposed.[46] Metal nanoscale structures (notably from Ag or Au) provide the most enhanced signals for surface-enhanced Raman scattering (SERS) thus improving both detection limits and speed of SERS-based detection of food-related analytes such as melamine and perchlorate or food-borne pathogens including virus and bacteria like *Salmonella*.[40] Funtionalized paramagnetic nanomaterials are often used to bind and concentrate pathogens or compounds present in foods. Adsorbed antibodies provide molecular recognition, thereby reducing interferences from other food-borne pathogens and improving detection selectivity.[40] There are many examples of nano-enabled devices that detect water and airborne pathogens, toxins, and contaminants in foods and on food packaging or food processing surfaces.[26,41,44,47]

Another advantage is that nanoprobes aim to operate using significantly reduced sample volumes and fewer sample preparation steps compared to traditional techniques, while still providing low detection limits for water- and food-relevant analytes. For example, Peng *et al.*[41] used stacked Au nanorods with surface-enhanced Raman scattering spectroscopy for highly sensitive detection of melamine and phthalates in aqueous samples. They were able to rapidly detect phthalates directly in a 10 μL orange juice sample at sub-femtomolar (0.9 fM) concentrations without the need of sample pre-treatment steps such as extraction, pre-concentration or derivatization required by current techniques such as HPLC, mass spectroscopy or colorimetric methods. Liu *et al.*,[48] used anti-body coated superparamagnetic nanoparticles to selectively detect *Vibrio parahaemolyticus* in shrimp in 4.5 h (relatively quickly compared to culturing and rtPCR methods) with a detection limit of $\sim 10^2$ CFU g^{-1}. The functionalized magnetic NPs use attached antibodies to provide high selectivity for the *Vibrio parahaemolyticus*, and they act to concentrate the sample while the paramagnetic properties enable sensitive magnetic detection through a lateral-flow immunochromatographic assay.[49] More recently, Park and Choi improved on this technique by incorporating an enzyme-modified silica NP as a label, achieving detection of *Vibrio parahaemolyticus* in oysters at $\sim 10^1$ CFU g^{-1} within 2.5 h.[50] This type of nano-enabled immunoassay can provide rapid, on-site, preliminary testing of pathogens in food and can be less expensive and less time-consuming than traditional culturing or PCR methods.[35]

The development of nanoprobes for detection of pesticide residues, antibiotics, mycotoxins, microbial contamination, plasticizers (phthalates), melamine, food spoilage or vitamin analysis in foods are already mature areas of research[26,27,30,32,35,37,40,41,44,51–60] that have produced some commercially available platforms (*e.g.* the "Nano-Bioluminescence Detection Spray" by AgroMicron for microbial detection (*Salmonella* and *E. coli*) in food using a luminescent protein; or the nano-enabled electronic tongue sensitive to compounds released by spoiling food for inclusion in "Smart packaging systems" by Kraft Foods). Nanosensors may ultimately provide the next generation of time and temperature sensing information systems needed to accurately monitor food quality and shelf life. Real-time, comprehensive data on water or food quality will allow faster responses to contamination or damage and enable more effective mitigation actions.[27]

Despite some commercial successes, achieving selective and sensitive detection of pathogens and toxicants, while minimizing interferences in complex food matrices remains challenging. The ability to distinguish between viable (infectious) and inert/dead pathogens amongst a large background of pathogenic organisms is another important challenge that must be overcome.[61] Gains in sensitivity of nano-enabled devices due to the miniaturization capacity must also be associated with reasonable costs as well as short measurement times and avoiding the need for extensive sample pre-treatment or pre-concentration steps. Manufacturing both nanosensors and nanoprobes is challenging as it requires the ability to manipulate individual nanostructures as well as the capacity to deal with agglomeration and aggregation, interactions with other components and interferences from ambient conditions.[27] Field deployment and validated field testing of nanosensors is generally lacking. Nanosensors for soil quality and field-scale systems for plant disease diagnosis remain to be tested in natural systems under realistic field conditions, and considerable additional research on sensor deployment techniques is necessary.[28] This is in part due to concerns over public safety and acceptance of nanotechnologies in foods.[27] Also, considering the shear mass of food that is

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processed each day, scalability as well as cost effectiveness must be achievable.

Nanotechnologies for pathogen control

Food loss (pre- and post-harvest) and food waste in Europe, North and Latin America, industrialised Asia or North-Africa account for large inefficiencies in agriculture. It is estimated that 30–50% of food supply is wasted in Europe and North America[62,63] at all levels of the value chain: in consumer households, retail establishments, food processing, and on the farm. Thirty one percent of the 2010 United States post-harvest food supply was estimated to be wasted at the retail and consumer level, resulting in economic loss on the order of USD$160 billion.[64] Food waste is often a result of spoilage from the activity of bacteria and fungi or from the presence of toxins and contaminants. Ensuring food safety requires the ability to control pathogens and allergens on foods all along the farm-to-fork continuum.

Fig. 2 summarizes the nanoscale properties leveraged and benefits of nanotechnology applications for pathogen control across the food production chain. These applications include control of airborne and waterborne pathogens (and human infectious agents), spoilage microbes on food crops, fresh produce, and animals, and for disinfection of contaminated surfaces where food is processed and prepared.[65–72] As shown in Fig. 2, the high surface to volume ratio of nanomaterials can improve the efficacy of disinfection through increased ion release (*e.g.* silver ions), greater photocatalytic activity (higher light absorption and quantum size phenomena) can improve antimicrobial efficacy, and the ability to functionalize surfaces of NPs with *e.g.* antibodies can provide selective targeting to specific pathogens.[72–74] One unique example include nanosized water droplets that contain hydroxyl radicals from electrospraying that have long lasting antimicrobial effects on food and food preparation surfaces.[72–76] More commonly, titanium dioxide is used nanoparticle for pathogen control due to its photocatalytic capacity to generate reactive oxygen species (ROS) upon irradiation.[21,77] Also, the bactericidal activity of metallic nanoparticles such as AgNPs or ZnONPs (which has been associated with the capacity to cause bacterial cell damage or generate ROS) is often used to produce antimicrobial surface nano-coatings.[72,77]

In general, nano-based antimicrobial platforms include nano-enabled food packaging systems which can provide long-term protection throughout transport and storage (for example preventing adhesion of pathogens to food surfaces, developing antimicrobial or antiviral surfaces or even light activated and self-cleaning surfaces) and also significantly extend the shelf-life of food.[26,56–58,72,78,79] Nanotechnology can produce antifouling surfaces by acting on the superficial topology to reduce the area available for bacterial adhesion or to generate nanostructured superhydrophobic surfaces.[72]

Commercial applications of nanotechnology already exist in retail food packaging (most commonly for fruits or vegetables).[25,44,55–59] These include packaging with better mechanical and physical properties, flexibility, durability, stability against temperature and moisture changes; "active" packaging (incorporating nanomaterials with antimicrobial or other *e.g.* antioxidant properties); nano-coatings (*e.g.* nanomaterials attached to the surface to improve barrier properties, surface biocides, antimicrobial and self-cleaning food contact surfaces); and "smart" and "intelligent" packaging (*e.g.* incorporating nano(bio)sensors to indicate quality of foodstuffs or nano(bio)switches to release food preservatives).[56]

There are a number of scientific and engineering implementation challenges for the implementation of nano-based antimicrobial agents and nano-enabled solutions for food safety. First, mechanisms involved in disinfection and pathogen inactivation processes must be fully understood. Although significant efforts have been made to explain inactivation pathways and efficiency of nanoparticles such as TiO_2, MgO, ZnO, Ag, CNT, fullerene derivatives, Al_2O_3 or zero valent iron there are still unknowns regarding the actual antimicrobial mechanisms (*e.g.* to fully distinguish between toxicity from the release of toxic ions and nanoparticles direct activity). The influence of environmental factors (*e.g.* light, pH or temperature) or interferences from matrix components (*e.g.* salts or natural organic matter) on disinfection efficiency have not been fully elucidated.[77] Second, the safety of nano-enabled packaging and products used directly on foods and food processing equipment must be verified to avoid any unintended negative consequences of their use such as leaching into the food or other user exposures. A critical safety aspect is the development of tools to assess potential hazard of nanomaterials by oral exposure and to fully characterize exposure routes.[55] The validity of currently used toxicological assays to estimate consumer oral exposure to nanomaterials are not fully vetted, particularly in light of possible "deviant" interactions and toxicokinetics in complex matrices, the broad range of exposure pathways, or effects associated specifically to size or nano-specific surface chemistry. Analytical tools to characterize nanomaterials in food matrices as well as to establish relevant dose metrics for interpretation of risk assessment studies are still needed. Public perception is another important factor that can hinder the realization of nanotechnology opportunities in the food industry. The safety of new materials to workers and consumers, and the impacts of nanomaterials on food quality must be determined and be acceptable to consumers. Nanomaterials used in foods and food packaging should also be reusable, recyclable, and/or biodegradable where possible. To promote adoption of nanotechnologies in foods, effective risk communication and management tools need to be developed and deployed to avoid public mistrust as was observed with genetically modified organisms/foods. Finally, regulatory challenges surrounding the safety and acceptance of nanotechnologies for food production, handling, transport, and storage must be addressed in the development stage so as to promote safe design principles.

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Membrane and sorbent technologies for distributed water treatment and efficient resource recovery

Robust distributed water treatment provides the ability to utilize a wider range of water sources (*e.g.* re-use of agriculture runoff) and can address problems associated with limited water supply, water pollution from agriculture runoff, harmful water-borne infectious illnesses, while improving conventional energy- and chemical-intensive decontamination processes (*e.g.* chlorination and ozonation).[80,81]

Fig. 2 summarizes the nanoscale properties leveraged and benefits of nanotechnology application in the development of membranes with greater selectivity, more selective sorbent technologies, more efficient separation systems and nano-enabled disinfection mechanisms for distributed water treatment and efficient resource recovery. Key opportunities for nanotechnology to make water more available, as well as less costly and energy intensive include the ability to specifically tailor water treatment systems at the nanoscale for greater efficiency in solar-driven processes;[21,82] improved membrane permselectivity for higher water recovery rates and lower energy consumption;[83] improved sorption capacity by superparamagnetic materials;[21] lower rates of membrane fouling;[83–85] and developing more resilient membranes and new membrane geometries *e.g.* by atomic level control during nanoscale manufacturing.[21] The nano-engineered fabrication process allows tailoring of membrane's wettability, surface roughness, electric charge, thickness and structures which compared with conventional fabrication methods (*e.g.* phase inversion) can increase the water flux and the rejection of contaminants (*e.g.* oil or surfactants) and lower the fouling ratio.[86] Improving membrane permeability will allow for smaller, more economically feasible distributed treatment systems, while tailoring surface properties is critical to moving contaminants of concern to selective deactivation sites.[21,80,81]

Nanomaterials can improve the removal efficiency of contaminants from water and lower associated energy requirements,[87] and operate where conventional chemical or reactor based systems are ineffective. For example, nano-enabled direct solar membrane distillation allows localized surface heating (by using light absorbing black nanoparticles that induce plasmonic resonance processes and generate localized heating) and it has the ability to capture a broader solar spectrum (*e.g.* utilize visible light rather than UV light) requiring less energy than conventional thermal membrane distillation.[88] Carbonaceous nanomaterials can provide multifunctional water treatment membranes exhibiting ultrahigh water flux values due to low frictional water flow through their carbonaceous pores.[89] Protein-polymer biomimetic membranes, aligned carbon nanotube membranes or thin-film nanocomposite membranes can also lower the energy requirements for nanofiltration (NF) (by enhanced water flux and separation capacity for both inorganic salts and small organic molecules in charged surfaces resulting from the dissociation of ionizable groups in the membranes), and improve control over NF membrane properties during synthesis (*e.g.* through improved interfacial polymerization incorporating nanoparticles and other additives, UV grafting/photografting, electron beam irradiation, plasma treatment and layer-by-layer modification).[21,77,85,90–93]

Nanomaterials offer great potential for resource recovery. Agricultural waste streams exist across the entire supply chain and contain valuable embodied resources. Separating the nutrient-rich wastewater fractions and recycling them as fertilizer can save valuable resources as well as energy. Key opportunities for nanotechnology to recover resources within the agri-food value chain and to reduce net life cycle resource inputs and impacts on the environment include nutrient recovery from leachates and runoff using highly selective membranes, adsorbents, and paramagnetic materials; water recovery from leachates and runoff using membranes selective for specific cationic and/or anionic species, reactive adsorbents for pesticide removal, and energy recovery from plant residues and animal wastes using novel catalysts to remove oxygen from biomass.[20,21,94,95] These technologies leverage nanoscale features including surface patterning and functionalization to provide controlled access and selectivity of solutes or macromolecules to tailored surfaces of nano-enabled adsorbents; shorter intraparticle diffusion distance; specificity of photocatalytic reactions that may be used to transform materials of interest or inactivate pathogens; and paramagnetic properties to enable sorbent recovery (Fig. 2).

Nano-enabled adsorbents (*e.g.* CNT, metal-based or polymeric nano-adsorbents, zeolites) designed for resource recovery must exhibit high selectivity, high adsorption rates, limited persistence, and some mechanism for reversibility so that nutrients captured from water can be subsequently released. It should be noted that superparamagnetism, as observed in nanomagnetite, is often used as a means to readily recover sorbents from water.[21] The inclusion of a nanomagnetite core into any sorbent material allows for easy separation of the sorbent from water under an applied magnetic field.

In case of intended water re-use for agriculture, it may be more desirable to leave nutrients in the water while selectively managing salinity and removing pesticides.[96] Most current separation processes for dissolved ionic species favor removal of multivalent species first, followed by monovalent removal. In contrast, the desired outcome would be to remove some monovalent species (*e.g.*, Na, Cl) while leaving behind other monovalent (*e.g.*, NH_4) and multivalent species (Fe, Ca, PO_4). The production of self-assembling nanostructures (*e.g.* for nano-enabled membranes) by means of the self-assembly of block copolymers has also been used to feature specific taylor-made characteristics for more efficient separation (*e.g.* high density cylindrical nanopores for enhanced selectivity and permeate efficiency).[81] Nanomaterials are also used to make more effective electrodes for capacitive deionization of wastewater.[97,98]

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Recovering cellulosic wastes as a potential feedstock for biofuel production is also a good opportunity for nanotechnology solutions. Homogeneous thermolysis of biomass-derived macromolecules within woody biomass and/or grasses involves thousands of reactions producing a mixture of hundreds of compounds referred to as bio-oil. The heteroatom content of woody biomass and bio-oils (biomass with O-levels ~50 wt%) requires new catalysts for removal of oxygen from biomass. There are examples of applications of nanotechnology in pyrolysis and hydrogenation, gasification, transesterification or in the design of high performance catalysts (*e.g.* supported by carbon nanotubes) for reforming of biomass-derived compounds.[20,94,95,99]

Relevant challenges for nanotechnology applications in water treatment systems relate to testing and validation in real systems with complex water and wastewater matrices. Most nanotechnology applications in water treatment are still in the stage of laboratory research. However, there are a few pilot and field tests and several commercially available nanotechnologies for water treatment or resource recovery (*e.g.* nanoadsorbents, nano-enabled membranes, nano-photocatalysts or nano-enabled disinfection systems). There is insufficient understanding of how potential catalysts or sorbents perform in the presence of high and variable organic carbon and biomass. Achieving selectivity for specific compounds (*e.g.* by tailoring atomic structures) remains challenging. Also, the high organic loading in agriculture waste streams makes it challenging to apply advanced membrane separation techniques due to anticipated rapid biofouling (although nanotechnology solutions have been proposed to prevent biofouling as described above). The scale-up of direct solar-driven distillation processes will require more effective light management (capacity to deliver light to water treatment reactors).[88] Also, although CNT or metal-based nanoadsorbents are commercially available and exhibit advantages over non-selective adsorbents (*e.g.* activated carbon or ion exchange) their use for wastewater treatment at an industrial scale is still often prevented by high production costs.[81] On the other hand, nano-enabled water treatment technologies can be more easily and cost-effectively incorporated into point-of-use scale systems (*e.g.* devices for purifying drinking water).[88] Better understanding and communication of potential risks, as well as long-term performance and efficiency testing of new nano-enabled technologies, are also limited. An essential question is whether or not nano-enabled applications can in fact be exploited to yield reductions in cost, or improvements in performance over currently available technologies.

Materials for controlled and targeted delivery of agrochemicals

Fig. 2 shows the nanoscale properties leveraged and benefits of nanotechnology application in targeted delivery of agrochemicals for improved crop yields and nutrition. Several unique properties of nanomaterials can be leveraged to enable the targeted and controlled release of agrochemicals, to increase the solubility and stability of active ingredients during storage and application (*e.g.* nanoemulsions) and to prevent their premature degradation, leaching or volatilization (*e.g.* by nanoencapsulation).[100] A highly promising opportunity for nanotechnology is the development of multifunctional nanomaterials for more efficient release of agrochemicals and targeted delivery of pesticides, biological materials or bioactive molecules (such as DNA, proteins, enzymes). Nanoformulations can contain multiple active ingredients and can be synthesized and formulated for strategic, timed and stimuli-responsive release (*e.g.* based on a carrier with controlled mobility and target selectivity) taking advantage of the high surface to volume ratio of nanomaterials and of their surface functionalization potential. The targeted and controlled release of agrochemicals will provide more efficient nutrient delivery and pest management and decrease both the dosage and loss of nutrients and pesticides, thus reducing soil and water pollution leading to both environmental and economic gains. Energy inputs can also be decreased as fewer chemical applications to crops and less irrigation will be needed. The small size of nanoparticles allows them to act as carriers of bioactive molecules into the plant vascular system through foliar or root absorption. Although the pathways for the actual uptake of nanomaterials by plant cells are not fully understood yet, there are reports of (insoluble) nanoparticles being taken up and translocated inside plants.[101] Nanoencapsulation of pesticides (*e.g.* polymer-based or lipid-based nanoencapsulation or using a porous inorganic nanomaterial as carrier) is able to prevent premature degradation of the active ingredient or increase their activity against pests for a longer period through controlled release.[100] The antimicrobial properties of nano CuO applied foliarly to eggplant resulted in increased resistance of the eggplant to a soil fungus and increased yields compared to unamended plants, even though the CuO NPs didn't kill the soil fungus.[102] Presumably, the small size and solubility of the CuO NPs aided in their foliar uptake and helped plants to better tolerate the soil fungus. The addition of CeO_2 to soils increased the salt tolerance of Canola, resulting in higher biomass production in salt stress condition compared to unamended soils.[103] These latter two examples show promise for selected metal oxide nanomaterials to improve crop production, but the mechanisms behind the greater plant health are not yet known.

There is a recent and growing body of literature on development of nano-enabled formulations for agrochemical delivery.[6,7,28,44,104–113] Compared to conventional agrochemicals, nano-enabled products have higher surface area, increased activity and mobility and lower solvent use in their formulations.[6] Nanomaterials in plant protection products are used either as active ingredients (*e.g.* SiO_2, TiO_2, Ag, Cu or Al nanoparticles) or as additives acting as controlled release carriers, protective/dispersing/biodelivery agents or photocatalysts.[107,110] Most published work is focused on increasing the solubility of the active ingredient through the

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use of microemulsions, nano emulsions, and nano-dispersion, and some products are commercially available (*e.g.* Banner MAXX, from Syngenta).[7,44] Potential mechanisms for controlled delivery of agrochemicals by nanomaterial carriers include adsorption or ligand-promoted attachment of active ingredients onto nanoparticles; encapsulation in nanoparticle polymeric shells or entrapment in polymeric nanoparticles.[7] The key function that these formulations provide is that only part of the active ingredient is immediately available. Prolonged release of an agrochemical from a nano-enabled product is achieved by diffusive mass transfer, chemical degradation (*e.g.* hydrolysis) or microbiological decomposition of the carrier, or controlled absorption of water leading to swelling of the carrier and subsequent dissolution and diffusion of the active ingredient to the exterior.[7,105] Natural, biodegradable, nanostructured polymers and polymer-nanohybrids are ideal materials for creating innovative formulations that provide targeted and triggered release of active agents such as pesticides, micronutrients, nitrogen, phosphorus, and potassium (N, P, K), and biological active molecules.[7,101,104–111]

Despite being a highly active research field, methods to provide targeted delivery to organisms through the use of biological materials (*e.g.* antibodies), or to make materials responsive to important environmental stimuli like moisture, pH, or light, are generally lacking. However, advances in the biomedical industry to create pH and moisture responsive materials for targeted drug delivery are recently being used for delivering agrochemicals. For example, chitosan and alginate-based nano-enabled delivery systems for pesticides have been proposed.[6,109,114–116] Most reported studies test the release of active ingredient in water only, and do not fully explore their efficacy in soils or assess the effects of environmental factors that may affect performance (*e.g.* pH, salinity, organic matter, microbial activity).[105,109]

Several challenges currently prevent implementation of smart nano-enabled agrochemicals. The nature of plant-nanomaterial interactions is not yet fully explored. It is uncertain what material formulation aspects are needed to optimize plant growth and to increase crop yields and the nutritional value of foods in a cost-effective manner. Areas for research include design and formulation of materials—including the effects of properties such as size, shape, surface structures, and composition on selective targeting and bio-uptake. There are challenges in creating formulations that can be effective in different soils and for a range of species-specific plant characteristics. Processes allowing nanoparticles to pass through cellular membranes and cell walls, as well as growth-enhancing mechanisms attributed to certain nanomaterials (*e.g.* carbon nanotubes), need to be clarified. Mechanisms and chemistries for targeted delivery must be developed. It remains unclear whether biological modes of targeting or physical/chemical modes of targeting (*e.g.* increasing availability of an active ingredient as a response to pH, moisture or temperature) are the best overall approach with respect to greatest efficiency and safety of use. Models to describe nano-enabled pesticide release under a range of environmental conditions as well as to evaluate toxicokinetics and toxicodynamics are still to be developed.[107] The ability to produce these materials on a commercial scale and to stabilize/prepare them for field applications still poses significant challenges. Biocompatibility and biodegradability aspects of nano-enabled carrier materials for agrochemicals need to be further examined. Mechanisms for the increase in plant biomass production or improved disease resistance associated with the use of nano-enabled fertilizers must be further understood. Mechanisms for direct plant uptake of nanoparticles as well as cell internalization, translocation and localization of nanomaterials in crop plants are not fully understood (there are relevant knowledge gaps particularly regarding the role of plant anatomy, the measurement of uptake rates and the definition of size exclusion limit) and very little information is available on the influence of environmental factors or of interactions between nanomaterials and the mucilage surrounding the roots or roots hairs.[101,110,117] Also, very few studies have investigated the fate and behavior (*e.g.* mobility and transformation) and the effects of nanomaterials in natural soils under environmental conditions. Methods are needed for tracking organic nanomaterials (in particular) in soil and plants, as well as for tracking their fate and degradation products in order to avoid phytotoxicity or potential residue carryover in food. Finally, the effect of nanomaterials in nano-enabled agrichemicals on food quality has not been determined.

Platforms for monitoring and improving animal health

Animal husbandry consumes an enormous share of the water and energy resources devoted to food production; for example, beef is estimated to require 3000–20 000 L kg^{-1} of water for production depending on the specific system design (industrial systems *vs.* grazing).[118,119] With meat consumption increasing globally in step with rising living standards,[120] reducing the resource requirements for animal product production is needed for more sustainable agriculture.

Fig. 2 summarizes the nanoscale properties leveraged and benefits of nanotechnology opportunities to improve animal health. Nano-enabled delivery of (micro)nutrients, antioxidants, and supplemental nutrients can improve the efficiency of protein synthesis or delivery of cellulose enzymes for better use of energy in plant materials using micelles, liposomes, nanoemulsions, biopolymeric, nano lipid particles, and dendrimers.[13,14,25] These applications take advantage of solubility, high dispersability (*e.g.* in feed), high absorption and bioavailability or controlled release rates of specific nanomaterials, associated with the small size and high surface-to-volume ratio of nanomaterials.[13,25]

Nanotechnology also holds promise to improve both disease surveillance and control through "smart" targeted drug (vaccines and pharmaceuticals) delivery systems as well as detection and removal of pathogens or toxicants.[121–126] Various nanoparticles have been used for targeted delivery of

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anti-neoplastic agents, antimicrobials, analgesics, and anti-inflammatory agents.[127–130] Targeting was achieved through the ability of nanoparticles to accumulate at sites of increased vascular permeability (*e.g.* tumors, infections and areas of inflammation) or by functionalizing the surfaces of the nanoparticles with a targeting moiety.[122] Nano-based drug delivery also aims at increasing drug bioavailability through sustained controlled release of the active ingredient.[122] Common nano-enabled formulations for drug delivery include polymeric nanoparticles, solid lipid nanoparticles, liposomes, nano emulsions or micelles.[122] There are currently over 30 nano-based therapeutic products approved for clinical use in humans and at least 200 more under development.[122]

Nano-enabled imaging and diagnostic tools have also been proposed leveraging nano-specific optical properties as well as superparamagnetism of certain nanomaterials. For example, controlled linkages of functionalized nanoparticles to biological molecules (including antibodies, peptides, proteins and nucleic acids) are used for the detection of viral, parasitic and bacterial pathogens in veterinary medicine.[122–126] "Theragnostics" is a combination of diagnostics and therapy in a single step (the imaging agent is also an active ingredient) and it is also possible *via* nanotechnology.[13,14,121,122]

Finally, nanotechnology can enable more efficient and precise estrus detection and identity preservation and tracking in mammalian livestock to improve animal breeding and reproduction.[13,25] Trials of nano-enabled technologies for fertility testing and purification of bull semen for commercial artificial insemination have been developed.[131] These included nano-functionalization approaches to improve techniques such as sperm-mediated gene-transfer, loading sperm with exogenous proteins or sperm tagging.[132] A nano-enabled sensor for estrus detection has also been proposed.[133]

Key barriers to realizing nanotechnology opportunities for animal disease detection and surveillance center around identification of appropriately responsive nanomaterials for nanosensors and nanoprobes that are economically viable and environmentally benign with sufficient specificity to identify bio-targets, sufficient selectivity to overcome interferences, and sufficient sensitivity to detect relevant levels of targeted compounds. Realizing the benefits of sensors to improve animal disease or pathogen detection will require the identification of specific biochemical targets and multiplexing (systems integration) and pattern recognition.

Barriers and overlapping challenges

The unique properties of nanoscale materials enable their use in many ways that are different from conventional chemicals. Manufacturing these materials cheaply and safely, and designing them as selective, sensitive and durable for use in highly complex soil, water, food or waste matrices are the most significant scientific challenges to leveraging the high-value opportunities for nanotechnology to improve efficiency of agri-food systems. Future research should focus on addressing these challenges so that the benefits of nanomaterials can be realized.

Many of these applications also face engineering and technoeconomic challenges, including 1) slow technology diffusion in commercial and industrial applications; 2) uncertainty in the cost-to-value ratio of technology innovation in the low-profit margin spaces of water, agriculture, and energy; 3) safety and public perception concerns when utilizing nanomaterials in water or food systems; and 4) life-cycle issues associated with nanomaterials, including manufacturing of nano-enabled structures, sustainably fabricating nanomaterials at large scales, recovering nanomaterials from matrices, biodegradability and recyclability of materials and perceived risks of engineered nanomaterials in food and the environment. These challenges will need to be addressed in the design phase of any nano-enabled application requiring an innovative leap in nanomaterial design. While synthetic pathways to obtain nanomaterials with controlled structures and physical/chemical properties have been elucidated, we have not yet established relationships between specific material features and the elicitation of a given desired response. Establishment of these relationships is critical to realizing next generation nanotechnologies, including the proposed multifunctional platforms for the aforementioned applications.

The capacity to engineer and produce multicomponent structures at the nanoscale and to ensure their functioning under variable environmental conditions is particularly challenging. Leveraging the advantages of high surface-to-volume ratios of nanoparticles which enable rapid, and often reversible, reactions (relevant for improved sensing, pathogen detection, disinfection, controlled release of agrochemicals, water treatment or resource recovery) requires the capacity to ensure that nanoparticles come into contact with target organisms, surfaces, analytes or pollutants within a specific soil, plant, food or water matrix.[27,88] The development of such capacity is complex and often associated with the use of carrier materials (*e.g.* porous inorganic nanomaterials such as mesoporous silica nanoparticles), nanoencapsulation (*e.g.* polymer- or lipid-based encapsulation), or scaffolding (*i.e.* embedding nanoparticles into macroporous hierarchical structures).[88,100] Providing these carrier materials or structures with external stimuli-response capacity is critical for targeted and responsive release or delivery of nanoparticles. Although these processes are reported in the literature,[106,134–136] actual products have been slow to mature beyond the laboratory-scale into larger-scale.

Costs and capacity needed to develop or access the nanotechnology are critical aspects for the realization of the above discussed opportunities. Many recently developed nano-enabled systems in the food or water industry are proprietary and since development and production costs are not disclosed, an effective comparison of costs with conventional systems is not possible.[55] Generally, costs and technical barriers for the incorporation of nanomaterials in already existing technologies (*e.g.* for food packaging or free

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dispersion of nanoparticles in bulk water for water treatment) or for the use of nanomaterials as additives in conventional product formulations (*e.g.* agrochemicals) are expected to be relatively low and easier to overcome than developing novel technologies. In certain cases (*e.g.* surface nano-coatings applied in multi-layer deposition processes, coatings produced using plasma technology or sol–gel processes) high costs still hamper the scale-up and widespread use of such nano-enabled technologies.[55,88]

Concerns regarding labelling, product safety, health and environmental consequences or manipulation of foods also significantly hinder consumer acceptance of nano-enabled foods.[40] This is aggravated further by the lack of comprehensive risk assessment and regulatory frameworks and unknowns regarding the way nanotechnology in the food sector will be handled by regulatory agencies in the future, particularly considering that for several cases, potential risks are still under evaluation. Thus, design, production and commercialization strategies for nano-enabled technologies must fully take into account concerns and risk perception by consumers and possibly include effective risk communication aspects.

"Smart" packaging and quick systems for detection of pathogens and food contaminants appear to be segments of the agri-food market that more readily recognize the benefits of nanotechnology. Proven successes in these sectors in the next few years could provide confidence in nanotechnology, help to drive-down materials costs, and promote applications in other niche markets of the agri-food industry.

Finally, tools are needed to better perform techno-economic gap analyses at the integrated systems level, and to integrate research outcomes across disciplines and sectors with value-based decision-making support. Stakeholders should be brought into the process early on to clarify in what ways data will be used to maximize public benefit of new technologies while minimizing undue hardship on agricultural producers. There is a pervasive need for qualitative, quantitative and communication based tools to support regulatory and social acceptance of nano-enabled technological solutions for food and water applications. Managing risk perception by consumers and manufacturers, and overcoming the regulatory challenges to implementing these new technologies is also essential to their successful adoption.

Conclusions and outlook

This tutorial review provides the basis for identifying future priorities and challenges for leveraging nanotechnology opportunities to promote sustainability of agri-food systems. Most particularly:

- Nanosensors and nano-enabled platforms for pathogens detection are highly cross-cutting technology development opportunities across the farm-to-fork continuum.
- Nano-enabled "smart" and/or "active" food packaging and nano-based anti-microbial platforms for long-term protection of foodstuffs is currently one of the most mature opportunities for nanotechnology in agri-food systems.
- Innovative nano-enabled methods for targeted and timed release of agrochemicals (pesticides and/or nutrients) or pharmaceuticals are promising, but a great deal of research is still necessary to realize this opportunity.
- Selectivity, sensitivity, robustness and ability of the materials to work in complex matrices/systems are essential barriers to overcome.
- Long-term efficiency of the nano-enabled technologies under natural/field conditions must be evaluated and risk assessment protocols and guidelines must be revised to account for specific properties of materials used in nano-enabled applications.

The potential of nanotechnology to improve sustainability at the FEW nexus presents tremendous opportunity, but it will require substantial investments in research and development, as well as serious efforts to gain regulatory and public acceptance of the benefits of the approach, particularly regarding application in foodstuffs.

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