

Review

A Review of Metal and Metal-Oxide Nanoparticle Coating Technologies to Inhibit Agglomeration and Increase Bioactivity for Agricultural Applications

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Received: 23 June 2020; Accepted: 12 July 2020; Published: 15 July 2020



Abstract: Coatings offer a means to control nanoparticle (NP) size, regulate dissolution, and mitigate runoff when added to crops through soil. Simultaneously, coatings can enhance particle binding to plants and provide an additional source of nutrients, making them a valuable component to existing nanoparticle delivery systems. Here, the surface functionalization of metal and metal-oxide nanoparticles to inhibit aggregation and preserve smaller agglomerate sizes for enhanced transport to the rooting zone and improved uptake in plants is reviewed. Coatings are classified by type and by their efficacy to mitigate agglomeration in soils with variable pH, ionic concentration, and natural organic matter profiles. Varying degrees of success have been reported using a range of different polymers, biomolecules, and inorganic surface coatings. Advances in zwitterionic coatings show the best results for maintaining nanoparticle stability in solutions even under high salinity and temperature conditions, whereas coating by the soil component humic acid may show additional benefits such as promoting dissolution and enhancing bioavailability in soils. Pre-tuning of NP surface properties through exposure to select natural organic matter, microbial products, and other biopolymers may yield more cost-effective nonagglomerating metal/metal-oxide NPs for soil applications in agriculture.

Keywords: metal/metal-oxide nanoparticles; nanoparticle coatings; capping agents; agglomeration; surface modification; rhizosphere; soil amendments; sustainable agriculture; bioactivity

1. Introduction

1.1. Nanoparticles in Agriculture

Nanoparticles (NP)s are increasingly being investigated for agricultural applications to improve crop yield and performance while reducing waste and runoff. Metal and metal-oxide NPs have been widely demonstrated to provide multiple benefits to plants through delivery of micronutrients, stimulation of plant defense mechanisms, and inhibition of plant-pathogens. The sub-100 nm size allows for greater reactivity, mobility, and uptake in the rooting zone of many crops; however, these same properties often promote NP agglomeration and strong adsorption to soil particles. This paper reviews specialized coatings on metal and metal-oxide NP formulations for the purpose of inhibiting agglomeration and promoting targeted application. Metal and metal-oxide NPs are widely explored in agricultural applications because they may supply essential elements as fertilizers, and at higher doses, as pesticides [1–7]. Nanoscale silicon dioxide, copper oxide, and zinc oxide can support crops against drought and alleviate heavy metal contamination [8,9]. NPs, defined as having at least one dimension smaller than 100 nm, offer a higher active surface area to volume ratio imparting greater reactivity

relative to bulky counterparts and tunable control over nutrient dissolution. The nanosize instills unique soil transport properties and enhances their bioavailability in crops [10–12]. However, due to their high surface area to volume ratio, and associated high surface energy, NPs often agglomerate under environmental conditions. Agglomeration can occur shortly after NP synthesis, after resuspension of a dry powder, or during storage and transport in aqueous suspensions. Even if NP size is preserved throughout transport, factors in soils and soil pore waters may promote further agglomeration after delivery. This can result in phytotoxic effects in plants, loss of material from runoff, or reduced efficiency due to the increased size, nonuniform soil distribution, and hindered transport [13–16].

NPs can be introduced to crops through foliar applications, seed treatments, or soil application. This review focuses on soil application of NPs and their resulting transformations including: (1) sorption to soil particulates; (2) secondary agglomeration; (3) dissolution or chelation; and (4) capping or complexing with soil minerals and dissolved organic matter (DOM) [12,17]. Soil additives can be introduced during tilling or planting, or as a direct application to seeds prior to planting. The DOM in soils comprises: humic acids and fulvic acids, fatty acids, proteins, low molecular weight carboxylic acids, phenolics and amino acids from plant exudates; and microbial and macrofauna byproducts. DOM coatings affect the charge and steric properties of NPs, influencing sorption, diffusivity, and dissolution [18–20]. Some coatings may increase bioactivity by promoting dissolution whereas others may passivate.

1.2. Effects of Soil on Fate and Transport

In soils, and especially near the rooting zone of plants, we anticipate the presence of sand, silt, and clay particulates, low molecular weight organic acids, amino acids, and discarded root cap cells [21]. This influences the pH, salinity, and readily adsorbed organic matter available in soils, and therefore the stability and dissolution of NPs into their constituent fertilizers or pesticides. In order to target the rooting zones of plants and serve as effective delivery vehicles, NPs must be stable in soil-like conditions while supplying metals or metal ions at a controlled nontoxic rate. The mass fraction of dissolved organic carbon (Figure 1A) and the pH of soils (Figure 1B) range widely across the globe but throughout the continental US tend to fall in the intervals of 2 to 100 per mille and 5.5 to 8 log units, respectively. Near the rhizosphere, sloughed root material significantly alters the carbon content and the pH can vary by up to 2 or 3 log units depending on the mechanisms of plant nitrogen uptake and modes of iron acquisition [22–24].

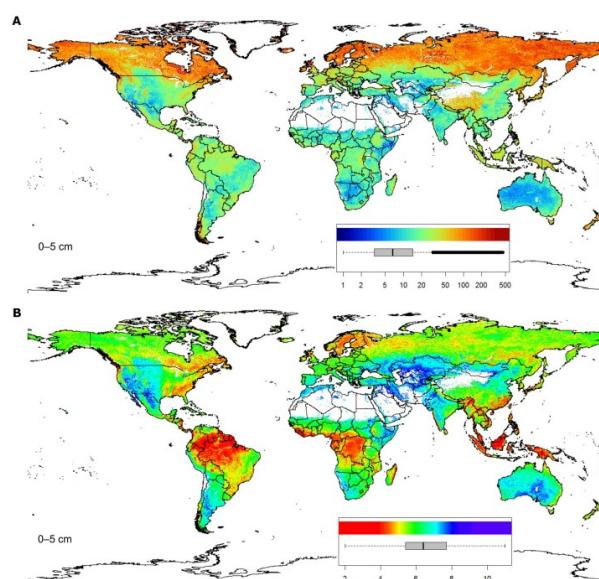


Figure 1. Modeling predictions for global topsoil profiles (0–5 cm depth) showing ranges of (A) the mass fraction of organic carbon content (per mille) and (B) the pH [25].

Soil pH influences the rate at which NPs dissolve into their constituent metals and dictates the speciation of the released metals within the soil, which can affect plant bioavailability. As illustrated in Figure 2, the free Cu ion rapidly decreases as the pH becomes alkaline. In sufficiently acidic soils, NPs may readily dissolve, but in more calcareous soils there may be limitations to NP efficacy without the use of a coating to promote dissolution. Gradients of mono and divalent ion concentrations in the rooting zone can also affect NP-soil interactions [26,27]. Charge screening can increase agglomeration or form ionic bridging between otherwise stable NPs. This can reduce the exposed surface area available for solubilization or plant-NP interactions. Agglomeration is also influenced by the effective surface charge, or zeta potential, of NPs. NPs exhibit a net-neutral surface charge at pH values near the point-of-zero-charge (PZC) where they become more susceptible to agglomeration. Greater NP stability is observed at a highly positive or highly negative zeta potential far removed from the PZC. As such, coatings designed to stabilize NPs through electrostatic repulsion must be adapted for a range of soil pH values and electrical conductivities. Zwitterionic or brush layer polymer coatings imparting steric repulsion may provide a broader means of discouraging NP agglomeration and attachment to soil particulates or DOM. As depicted in Figure 3, depending on soil properties and NP coatings (whether intentional or incidental), metal and metal-oxide NPs may become bound in inaccessible or unreactive forms that are unusable by plants.

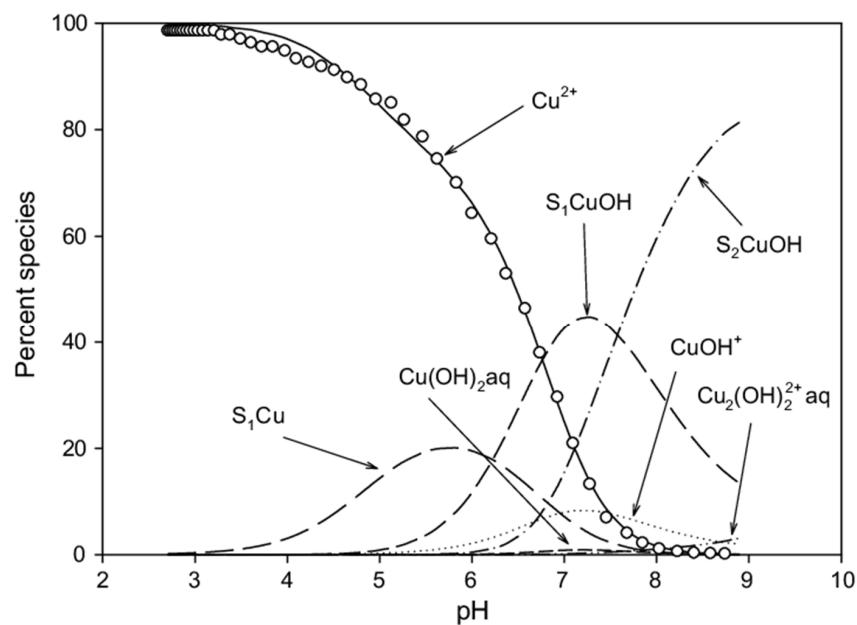


Figure 2. Example of the theoretical speciation curves for Cu species relative to pH [28]. Different Cu complexes can demonstrate varying degrees of solubility and accessibility to plants and plant microbes.

1.3. Agglomeration in Soils and Complex Media

Agglomerated NPs behave more akin to bulk counterparts, negating the inherent benefits of nanoscale materials. The increase in size alone can prevent NPs from being taken up by plants and translocated through the vasculature in the intact form [29–31]. Furthermore, agglomerates alter the surface properties of the NPs leading to complications when scaling up for field applications [32,33]. Changes in structure and morphology, such as irreversible gelation or uniaxial elongation can occlude transport pathways in plants [34–37]. Dissolution is slowed by agglomeration due to a reduction in exposed surface which consequently lowers the supply of nutrients to plants and the surrounding soil fauna. The size of NPs also plays a significant role in the fate and transport through environmental media as small NPs exhibit greater motility and spread more easily throughout ecosystems, whereas larger NP agglomerates are more readily bound to soil matter [38,39].

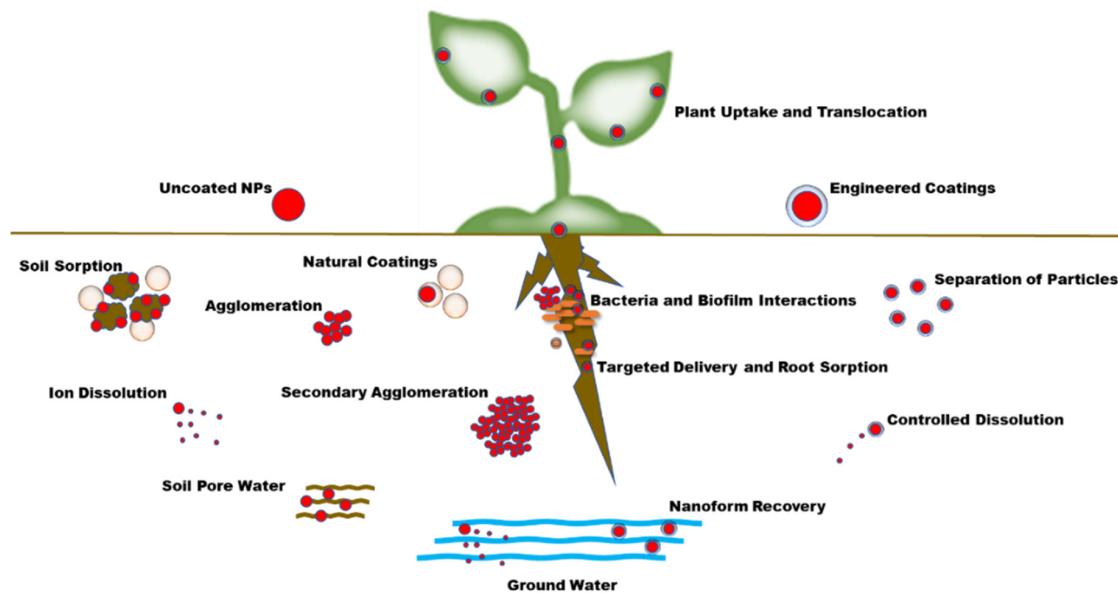


Figure 3. The use of protective antiagglomerate coatings can influence the efficacy of the application, fate, and bioavailability of NPs in soils and the environment.

1.4. Agglomeration during Storage and Transport

NPs must be prepared, stored, and transported before application. During this time, suspensions may become unstable, either precipitating out or agglomerating. The drying of samples for shipping imposes strong forces on the particles, potentially leading to sintering and irreversible agglomeration without the use of protective coatings [40–43]. When drying, there is initially a constant evaporation of solvent throughout the suspension; however, as drying continues, outer layers of solvent around the NPs will evaporate faster while solution trapped between NPs or agglomerates releases slower, thereby creating more interactive forces between particles [44]. This process can lead to plastic deformation and bridging across NPs resulting in further agglomeration [44,45]. Due to the nanoscale size of the particles these forces can onset even at lower temperatures for some NPs [44–46]. As a result, drying can influence the homogeneity and compaction of nanopowders, and ultimately their usability [40,44]. Therefore, coatings can play an important role in stabilization during the preparation, shipping, and storage of both suspended NPs and dry powders alike [46–50].

2. Coatings

Coatings are either physically or chemically adsorbed to the surface of NPs by hydrogen bonding, electrostatic forces, covalent bonds, or hydrophobic interactions, and can limit agglomeration or regulate dissolution. Coatings can be single layered, multilayered, or form brush or gel-like networks on the NP surface [51]. Changes in surface chemistry and modifications to NP zeta potential can impart stability via electrostatic repulsion and steric hindrance to core metal/metal-oxide NPs, inhibiting the onset of agglomeration [52–54]. Consequentially, the altered surface affinities can modulate NP interactions with plants, bacteria, or fungi providing opportunities for NP carriers with nutritional or antimicrobial payloads as multifunctional delivery systems for agricultural applications [12,55].

Coatings can be further tuned to alter NP surface charge, decorate NP surfaces with functional groups, or impart NPs with “stealth” surface properties leading to preferential adsorption and increased uptake in plants [56–58]. Coatings can modify the colloidal stability of NPs and screen against nonspecific binding by proteins and soil organic matter that would otherwise propagate bridging effects responsible for agglomeration and sorption. Colloidal stability also plays a vital role in the bioavailability of metallic NPs and their constituent ions; by regulating the release of ions or reactive oxygen species (ROS) through surface coverage, and by limiting exposure or adsorption of agglomerates, coatings can help mitigate the toxicity of metal-oxide NPs [59–61].

It is not always practical to apply coatings during complex NP syntheses but breaking down agglomerates through sonication can provide new windows of opportunity for introducing coatings [36,46]. Even without preserving the initial size of NPs after synthesis, limiting agglomerate size can be important in alleviating toxicity and sedimentation [62–64]. Coatings can help tailor the NP surfaces for a variety of specific agricultural applications as long as care is taken to mediate the bioavailability of NPs with consideration for plant and environmental toxicity [12–14,64,65].

3. Advances in Coating Technology

3.1. Review of the Literature

This review assesses state-of-the-art NP coatings for limiting agglomeration after synthesis, mediating dissolution of ions, improving delivery to the rooting zone, and enhancing bioavailability in crops. Sections will include factors influencing agglomeration and the role of NP coatings. The need for NP capping is addressed and comparisons are drawn between naturally occurring organic layers formed in soils and custom-engineered capping layers. Coatings are classified into four categories of focus where recent advances and new directions are highlighted. The literature was surveyed from Google Scholar and Scopus databases with the search terms including “NP” or “Nanoparticle” and “Coating” or “Capping”, both with and without the terms “Agriculture” and/or “Agglomeration”. Nearly 5000 articles were retrieved from the years 1990 to 2020. However, there are many variabilities in experimental parameters and testing environments, including pH, concentrations, solvents or buffers, and the instrumentation used to assess agglomeration, transport, and biological relevance. Published results were screened for inclusion using the following criteria:

- Use of spherical core metal or metal-oxide NPs;
- Coatings that fully or partially encapsulate NPs;
- Testing specifically for agglomeration under biologically relevant conditions;
- Agriculturally viable NP-coating systems.

For simplicity, this review has categorized common, state of the art coatings into four categories: natural organic matter (NOM) coatings, polymer coatings, zwitterionic coatings, and miscellaneous coatings. Table 1 provides an overview of this classification; however, a more interactive spreadsheet has been included as supplemental information (Supplementary file 1), which allows for searching of key terms, while subdividing classifications into individual sheets within the file. This may allow the reader to update the file with the latest outcomes in the area of metal and metal-oxide NP capping for agricultural applications.

Table 1. A summary of NP capping based on four major capping chemistry classifications. Dashed entries indicate values that were not reported by the authors. Approximations were estimated from graphs. Where multiple coatings were assessed, only the best performing coatings were included. An interactive, expanded summary table is provided as Supplementary file 1.

NP and Source Details			NP Size (Technique)			Surface Charge (mV)				Testing Conditions Where Stability was Observed				
Source	Coating (Classification)	Core NP(s)	Bare Size (nm)	Coated Size (nm)	Medium	pH	Bare NP Zeta Potential	Coated NP Zeta Potential	pH	Temperature	Ionic Stability	Biological Components	Organic Matter/Soils/Polymers	Time
Adeleye 2014 [66]	Soil Matter (NOM)	Cu, CuO, Kocite	40, 50, 50,000 (SEM) 2590, 280, 1532 (DLS)	~, 308, - (DLS)	0.5 mM PBS	7	-34	-25 (EPS) -45 (SRN)	4, 7, 11	-	1, 10, 100 mM NaCl	5 mg-C/L (EPS) 5 mg/L (SRN)	-	90 days
Baalousha 2013 [67]	FA (NOM)	citrate-Ag	29.9 (DLS) 17 (TEM) 20.8 (Flow-Field Flow Fractionation)	-	DI Water	7	EPM: -3.88 × 10 ⁻⁸ m ² /s	EPM: Reported as "Lower" in the presence of FA	~7	-	NaCl, NaNO ₃ , Na ₂ SO ₄ , CaCl ₂ , Ca(NO ₃) ₂ , CaSO ₄ , MgCl ₂ , MgSO ₄ , and NaCl/CaCl ₂	Very Soft Water, Soft Water, Sea Water	-	-
Dutta 2019 [68]	HA (NOM)	ZnO	30 (Sigma-Aldrich)	25 (SEM)	-	-	-	-	4, 7, 12	-	-	-	-	10 days (10 ppm HA)
	Citrate (Misc)	ZnO	30 (Sigma-Aldrich)	16 (SEM)	-	-	-	-	4, 7, 12	-	-	-	-	10 days (10 ppm citrate—performed worse than HA)
Estephan 2010 [69]	SBS (Zwitterion)	Silica	16.8–17.5 (SEM)	-	-	-	-	-	7.4	Up to 37 C	Up to 3M	50% FBS	-	15 days
Huang 2016 [70]	Cysteine Betaine (Zwitterion)	Au-Ag	40–100 (SEM/DLS)	102 (DLS)	-	-	-	-	7.4	Up to 55 C	Up to 3M	Gram positive/gram negative bacteria in 1% FBS	-	24 h
Jin 2009 [71]	HS-PC (Zwitterion)	Ag	7.8 (TEM)	7.8 (TEM)	-	-	-	-	7.4	Up to 37 C	Up to 2M	Various	-	24 h
Khan 2011 [72]	EPS (NOM)	Ag	~50 (DLS)	~70 (DLS)	DI Water	7	10.23	-29.32 (10 mg/L EPS) to ~ -42 (250 mg/L EPS)	~3–12	-	Up to 1 M NaCl	-	-	>72 h

Table 1. Cont.

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Source	Coating (Classification)	Core NP(s)	Bare Size (nm)	Coated Size (nm)	Medium	pH	Bare NP Zeta Potential	Coated NP Zeta Potential	pH	Temperature	Ionic Stability	Biological Components	Organic Matter/Soils/Polymers	Time
Liu 2011 [73]	HS-C10-SN4 (Zwitterion)	citrate-Au	16, 50, 100 (DLS/TEM)	~ 17.5, 55, 105 (DLS)*			-		1–13	37 °C	Up to 2M NaCl, PBS	DMEM + 10% FBS, Lysozyme, BSA, Plasma	-	6 month
	HS-PEG2000 (Polymer)	citrate-Au	16, 50, 100 (DLS/TEM)	~ 45, 80, 135 (DLS)*			-		2–12	37 °C	0.1 M NaCl, PBS	DMEM + 10% FBS	-	4 month
	Citrate (Misc)	Au	16, 50, 100 (DLS/TEM)	~16, 50, 100 (DLS/TEM)			-		7.4	37 °C	-	-	-	72 h
Lv 2014 [74]	HA (NOM)	CeO ₂	538.2 (DLS)	282.8 (5 mg/L HA, DLS) 249.1 (10 mg/L HA, DLS)	DI Water	7	-7.96	-33.58 (5 mg/L HA) -35.72 (10 mg/L HA)	7–10	-	Up to 0.1 M NaCl	-	Sand	-
	Random Copolymer MA/SBMA (Zwitterion) Block Copolymer MA/SBMA (Zwitterion)	Silica	22 (Ludox-40)	~180 (in water, DLS) ~350 (in brine, DLS)			-		-	Up to 90 °C	Water, Seawater, Arab D Brine	Up to 120k mg/dm ³ (3 types of electrolytes)	-	>30 days
Ranka 2015 [75]	Disulfide Zwitterion (Zwitterion)	citrate-Au	2.8 (QELS) 3.2 (TEM)	3.2 (QELS)			-		-	Up to 90 °C	Water, Seawater, Arab D Brine	Up to 120k mg/dm ³ (3 types of electrolytes)	-	>30 days
	Citrate (Misc)	Au	N/A	2.8 (QELS) 3.4 (TEM)			-		-	-	-	BSA, Lysozyme	PSS, PAA, PDADMAC, PAH, PVBTMAC	-
	Tebbe 2015 [77]	Albumin/Proteins (NOM)	Au	~80 nm (TEM) +Different aspect ratios	-	PBS, DMEM, NCS	7.5	-	-35 (pH 12) +20 (pH 1)	2–12	-	-	Up to 20 mg/mL biological media (PBS, DMEM)	-
Whitley 2013 [78]	PVP (Polymer)	Ag	51.4 (DLS) 53 (TEM)	51.4 (DLS) 53 (TEM)	DI Water	6	-24.7	-101 * -24.7 *	-	-	-	-	Soil, Sewer Sludge (1% and 3% w/w)	-
	Citrate (Misc)	Ag	51.4 (DLS) 53 (TEM)	84.4 (DLS) 84 (TEM)	DI Water	6	-24.7	-24.7 *	-	-	-	-	Soil, Sewer Sludge (1% and 3% w/w)	-

Table 1. Cont.

NP and Source Details			NP Size (Technique)			Surface Charge (mV)				Testing Conditions Where Stability was Observed				
Source	Coating (Classification)	Core NP(s)	Bare Size (nm)	Coated Size (nm)	Medium	pH	Bare NP Zeta Potential	Coated NP Zeta Potential	pH	Temperature	Ionic Stability	Biological Components	Organic Matter/Soils/Polymers	Time
Yang W. 2008 [79]	pCBA (Zwitterion)	Au	18.5 (TEM)	58.4 (DLS)			-		7.4	-	20% NaCl	Up to 100% BSA, 1 mg/ml Lysozyme	-	-
	PEG5000 (Polymer)	Au	18.5 (TEM)	53.4 (DLS)			-		7.4	-	-	-	-	-
	OEGMA (Polymer)	Au	18.5 (TEM)	74.3 (DLS)			-		7.4	-	-	-	-	-

* Values may be reversed—a discontinuity was observed between the graphs and text. Abbreviations: Bovine Serum Albumin (BSA), De-ionized (DI), Dulbecco's Modified Eagle Medium (DMEM), Dynamic Light Scattering (DLS), Electrophoretic Mobility (EPM), Extracellular Polymeric Substance (EPS), Fetal Bovine Serum (FBS), Fulvic Acid (FA), Humic Acid (HA), Methacrylic Acid (MA), Natural Organic Matter (NOM), Oligo(ethylene glycol) Methylmethacrylate (OEGMA), Poly(acrylic acid) (PAA), Poly(allylamine hydrochloride) (PAH), Phosphate-Buffered Saline (PBS), Phosphorylcholine (PC), Poly(Carboxybetaine Acrylamide) (pCBA), poly(diallyldimethylammonium chloride) (PDADMAC), Polyethylene Glycol (PEG), Poly(styrene sulfonic acid) (PSS), Poly(vinylbenzyltrimethyl ammonium chloride) (PVBTMAC), Polyvinylpyrrolidone (PVP), Quasi-Electric Light Scattering (QELS), Scanning Electron Microscopy (SEM), Sulfobetaine Methacrylamide (SBMAA), Sulfobetaine Siloxane (SBS), Suwannee River Natural Organic Matter (SRN), Transmission Electron Microscopy (TEM).

3.2. Natural Organic Coatings

Highly characterized, commercially available soil organic matter is used for the coating and protection of nanomaterials. Natural organic matter (NOM), dissolved organic carbon (DOC) and soluble humic acid (HA), or fulvic acid (FA) are natural, environmentally friendly surface coatings that may impart NP agglomeration resistance via added steric hindrance, increased electrostatic repulsion, and greater hydrophobicity [80]. It is expected that any NPs applied to soils will inherently develop some degree of natural organic coating; however, pretreating the NPs with such coatings enables finer tuning of the properties, preserving NP stability during transport and facilitating nanosized application at the time of introduction [81]. This can encourage more widespread delivery to the rooting zone and avoid pitfalls with aggregation such as loss of material to sorption or runoff into ground water [81].

Due to an accommodating chemical structure, HA is perhaps one of the most widely used natural organic coatings. There exist facile methods for the surface coating of NPs by HA, and in addition to providing steric stabilization, HA coatings can promote NP dissolution and plant nutrient uptake [20,82,83]. HA has also been shown to provide auxiliary benefits through heavy metal remediation and pollutant removal in wastewater treatment [84]. A study by Bian et al. reported initial increase in ZnO NP stability with coating by HA, but over time an increase in agglomeration was observed that they attributed to bridging between functional groups of the coatings [85]. Applied with appropriate concentrations and delivery timing, Dutta et al. demonstrated enhanced wheat growth at an early stage in the presence of ZnO NPs coated in HA relative to controls of noncoated NPs [68].

Oriekhova and Stoll examined FA coatings for stabilizing CeO₂ NPs and claimed enhanced stabilization in all simulated water systems while protecting against alterations in pH, but reported complexations in natural lake water [86]. Li et al. described mechanisms by which NOM coatings could prevent bacterial adhesion and also scavenge metals or ROS to reduce toxicity [87]. However, it should be cautioned that different soil factors have varying attachment affinity to NP surfaces and differ in performance during transport through soils or organic media because of NP destabilization at lower concentrations [88]. For preventative antiagglomeration coating, there may be value in taking advantage of the higher attachment affinity of HA over FA or NOM, but for model systems of natural coatings, appropriate concentration and fractionation of subgroups must be considered [89].

Soil transport often results in exposure to a wide range of bacterial products that can passively form coronal layers over NP surfaces, especially in the case of biogenically synthesized NPs [90]. Microbial cells in some biofilms readily uptake and process NOM suggesting potential secondary benefits of organic coatings for plant/bacteria nutrition or targeted delivery soil microbes [91]. NPs are stabilized when coated in extracellular polymeric substances (EPS) found in the biofilm matrix. Khan et al. demonstrated that EPS coatings formed around Ag NPs in aqueous environments significantly increased the zeta potential and thereby the stability of the NPs in solution [92]. Adeleye et al. used a similar technique with EPS derived from phytoplankton to control dissolution, stability, and fate of CuO NPs for agricultural delivery [66]. Coatings will affect the fate of NPs in soils where biofilms and microbial products are ubiquitous [93]. Tebbe et al. created albumin-coated Au NPs that remained stable under biologically relevant conditions, notwithstanding the process of drying and redispersion [77]. Venkatachalam also used phycomolecules to coat ZnO NPs with some success stabilizing the particles and simultaneously introducing a growth-promoting agent during delivery [94].

Other sources of organic matter such as repurposed sewage have also shown promise as versatile coating options with auxiliary benefits. Although not directly targeting crops, Magnacca et al. utilized biowaste-derived coatings to improve the adsorption of iron oxide NPs used for pollutant removal in wastewater streams [95]. Although soil, bacteria, wastewater, and plant derivatives can all provide strong coatings for stabilization, combining multiple factors may further enhance efficacy. Research by Chowdhury et al. suggests that hybrid complexes of both HA and bacterial byproducts can have a more significant effect on the surface deposition of NPs within a test matrix than either alone [96]. Nonspecific binding was reduced significantly when both capping agents were present. The future for

organic capping layers provides many opportunities for the design of new multilayered coatings with added benefits and stemming from alternative sources of NOM.

3.3. Polymer Coatings

Polymers such as Polyethylene Glycol (PEG), Polyvinyl Pyrrolidone (PVP), Polyvinyl Alcohol (PVA), Polyethyleneimine (PEI) can be physiosorbed onto the surface of NPs where the long carbon chains offer sufficient steric presence to deter NP-NP interactions. Tuning chain lengths and adjusting ratios of hydrophilic and hydrophobic repeat units can influence the mechanisms by which polymer coatings self-assemble onto NP surfaces [97]. However, with the addition of polymeric capping layers it is also important to consider the ecological impacts of the coating material. Some polymers may undergo biodegradation providing a carbon nutrient source for soil microbes but complete breakdown is not always possible, leading to the potential of contaminating soils with plastic waste [98,99].

PEGylation of NPs, or adornment with, by nanolayer(s) of PEG polymer, is a practice taken from biomedical applications. It has proven effective for stabilizing NPs while aiding in circulation throughout the body and improving cell permeability for imaging and treatment [100,101]. Although PEG alone is already a strong stabilizing capping agent, Bagwe et al. demonstrated that balancing PEG with octadecyl or carboxylate groups helped further reduce the nonspecific binding of silica NPs to glass substrates [102]. This may have possible implications for soil applications and the reduction of nonspecific binding to soil matter. Nevertheless, the stabilizing behaviors of PEG must be weighed against ecotoxicity. Not all microbes break down PEG in soils, so the environmental impacts must be compared against the effects of increased plant uptake and mitigation of particle decomposition or ion release [103,104].

Baumann et al. showed significant stabilization of iron oxide NPs by a different polymer, PVP [59]. After noticeable ingestion by daphnids, no negative effects were observed resulting from the high iron content or from the polymer itself. In contrast, other coatings tested, such as citrate, dextran or ascorbate, had more influence on ion release or ROS generation which contributed to multiple sources of toxicity in the crustaceans [42]. Research by Yang et al. investigated how the presence of cysteine or HA might influence the efficacy of PVP coating Ag NPs, as determined by deposition onto a silica substrate [105]. It was concluded that HA likely formed an additional stabilizing layer surrounding the PVP-coated NPs whereas cysteine served to exchange with the PVP producing a less effective coating, noting again the importance of considering the test matrix to which particles are being applied. For example, although the added stability may improve bioavailability in soils, PVP is also known to bind phenols which may ultimately be detrimental to plant health and should be accounted for [106].

PEI has also been used to regulate the size and extent of Au NP agglomeration for use in biomedical systems by controlling the secondary aggregation of agglomerates [107]. Nevertheless, toxicity must also be considered for this polymer coating [108]. Xia et al., for example, found that while PEI coatings improved cellular uptake of nucleotide and drug loaded silica NPs, longer polymer chains were cytotoxic [109]. Carefully balancing hydrophobic and hydrophilic polymer segments alongside chain length is key in reducing toxicity and may also allow for the formation of superior amphiphilic coatings [110].

3.4. Zwitterionic Coatings

Zwitterions are a specific class of polymer coatings distinguished by typically shorter chain lengths and a uniquely dimorphic charge profile. A zwitterion is a mixed charge variant of a polyelectrolyte; a net neutral molecule with opposing locally positive and negative functional groups [69,111]. These molecules can align electrostatically, facilitating a convenient one-pot surface deposition onto NP surfaces through “click chemistry”, allowing for more aqueous syntheses and reducing the need for additional reaction steps or toxic solvents [112,113]. This chemistry is complimentary to the often highly negative surface charge of metal and metal-oxide NPs in solutions or soil matrices well above their PZC [54,55]. As a result, zwitterions are often viewed as a greener alternative to PEGylation

and other plastic coatings sometimes associated with a more negative public image [108,114]. For some biomedical applications, zwitterion-coated NPs were also shown to provide targeted delivery of DNA and proteins with improved performance over PEG-prepared NPs [71,114].

The ability of zwitterionic coatings to prevent fouling in biomedical systems may offer translational strategies for agriculture. Zwitterionic polyphosphorylcholine coatings have been shown to inhibit fouling by bovine serum albumin and other bioproteins [71,115,116]. A poly(carboxybetaine acrylamide) coating inhibited agglomeration of gold NPs due to protein fouling while providing a surface coating that could be functionalized to reach target sites in the body [79]. Rouhana et al. made highly charged NPs using a disulfide zwitterionic ligand [76]. Sulfobetaine siloxane zwitterions display strong surface adhesion with high steric hindrance to out-perform other polymeric coatings in reducing metal-oxide NP agglomeration [69,111,117]. Sun et al. were able to control loading and dissolution from within mesoporous silica NPs using pH-responsive sulfobetaine-inspired coatings to enhance bioavailability and release [118]. Tuning the coating to respond to pH changes in the rhizosphere could prove an effective means of targeting NPs to plants.

Zwitterionic polymers containing the betaine structure are also appealing for agricultural use since betaine is an osmolyte in plants and bacteria [119,120]. Both polymer chain length and charge distribution influence interparticle agglomeration and ion bridging [121]. Noy et al. took advantage of polymer chain length to control the nanocarrier drug release and cytotoxic effects from a novel zwitterionic block copolymer [122]. Others synthesize zwitterionic coatings for stability in harsh conditions. Poly sulfobetaine methacrylate zwitterionic coatings preserve NP colloidal stability at high temperatures and salt concentrations that could respond to changes in pH [75]. Polymethacrylate and polymethacrylamide sulfobetaine zwitterions gave stability in a broad range of salinity, including conditions as extreme as 3 mM concentrations [123]. A zwitterionic cysteine coating did not show the degradation of PEG based coatings [70].

There is little difference in performance between negative and positive zwitterionic surface coatings, provided the coated NPs are sufficiently far from their isoelectric point; however, research by Liu et al. suggests that mixed charge zwitterions may provide even stronger surface attachment and enhanced stabilization over singularly charged coatings [73]. Nevertheless, the choice of coating should reflect the selection of NP surface, solution chemistry and intended application.

3.5. Miscellaneous Coatings (Inorganic Coatings and Small Organic Molecule Coatings)

3.5.1. Inorganic Coatings

Inorganic coatings are also considered for agricultural purposes. Some researchers are using core-shell NPs with a more stable outer shell or decorating/adorning their primary NPs with smaller NPs having a greater surface potential to reduce agglomeration. Both gold and silica make good candidates for core-shell NPs for their high solution stability and ease of surface functionalization [124]. SiO_2 in particular is conducive to one-pot sol-gel syntheses that can be tailored to produce highly uniform and monodisperse NPs or surface shells for a variety of applications [125–127]. SiO_2 NPs have been demonstrated to coat Au and ZnO NPs for enhanced stability [128]. Lee et al. have also showed experiments with SnO_2 NPs providing even further enhanced stability over SiO_2 [129], however addition of tin to soils would be more costly and less desirable. In contrast, silicon is considered important for plant growth and for strengthening the walls of the plants without contaminating soils [130].

3.5.2. Citrate

Citrate is commonly used as a reducing agent in NP synthesis and is thus often present as a residual coating; however, it may also be intentionally employed as a stabilizing agent. Judy et al. compared both citrate and tannate molecules to investigate uptake of gold NPs into crops via soils [131]. It was determined that both the nature of the coating and the type of crop played significant roles in the availability and uptake. Zhang et al. demonstrated that citrate coatings played an important role

in mitigating agglomeration resulting from the influence of dissolved oxygen species in soils [132]. Whitley et al. observed significant agglomeration in Ag NPs over a span of six months that was mitigated by the presence of both PVP and citrate coatings as evidenced by a greater fraction being measured in pore waters relative to soil binding [78]. However, it was found that preconditioning NPs by exposure to sewer sludge did negate the benefits of these coatings, implying that the full soil profile should be considered in designing an effective coating. Baalousha et al. noted a greater shielding effect against monovalent cations, and the formation of natural, sterically stabilizing capping by FA up to a critical coagulation concentration that protected NPs from agglomeration [67].

3.5.3. Other

Pokhrel et al. looked at coating Ag NPs with Trolox, DOC, and cysteine, and concluded that the extent of ion release, modulation of adsorption peaks, and degradation of NPs varied by coating to affect toxicity and uptake [133]. Research by Zhang et al. compared coatings made from sodium dodecyl sulfate (SDS), sodium dodecyl benzene sulfate (SDBS), Tween 80, and hexadecyltrimethyl ammonium bromide (HDTMA) on the efficacy of reducing not just inter-NP agglomeration but also heterogenous adsorption to soil particulates [134]. SDS was identified to have the strongest effect due to its highly anionic properties, but findings were strongly dependent on soil properties and soluble organic matter.

Small amino acids and osmolytes, although metabolically active, generally require functionalization or polymerization to increase chain length and steric contributions to stability. Poly-L-arginine and poly-L-lysine have been used for coating metal-oxide NPs but as seen with other polymer coatings, chain length has to be carefully controlled to preserve benefits both to bioavailability and NP stability [135,136]. Trehalose has been used to coat NPs with some success in biomedical applications for reducing agglomeration by cellular proteins [137]. NPs derived from trehalose have also demonstrated reduced interparticle agglomeration [138]. As trehalose is a known osmolyte in plants and microbes, it may merit further consideration as an NP capping layer with implications for drought and salinity tolerance [139].

3.6. Encapsulation

Encapsulation is another viable approach for coating NPs and shielding them against agglomeration. Unlike capping layers which are chemically or physically adsorbed to the surface of NPs, encapsulating layers comprise a bundle of smaller NPs. Encapsulated NPs have less exposure to the soil matrix until the outer shell degrades. NPs maybe encapsulated within an outer shell or integrated into a larger network. Hydrogel and sol-gel matrices work well for encapsulation [140,141]. Taking lessons from natural systems or translational technologies, single component or mixed chitosan/alginate encapsulations could be used with metal and metal-oxide NPs [142–144].

4. Summary and Future Directions

Currently, there exist many viable coatings that can help stabilize metal-derived NPs in aqueous environments and complex soil media. Coatings can be tuned to control the application, fate, dissolution, and bioavailability of the NPs, but reducing costs for economic viability will play an important role in the agricultural success of these NPs. There is no one size fits all coating for every application, but coatings may be implemented to mitigate the forces of agglomeration in the presence of high salinity, over time, or in the presence of proteins and organic matter that would otherwise facilitate increased growth in agglomerate size. For soil applications where pH can vary widely with location, and natural organic matter may be highly prevalent, it is important to consider coatings that are specific to target soils as well as crops. Potential toxicity of NP coatings and dissolution of both ions and constituent metals must also be considered. As with the core NPs, the dose makes the poison, and the bioavailable dose depends strongly on agglomeration, distribution, and dissolution within the soil, rhizosphere, and tissues of the target crop.

In general, there are several trends that are consistent in reducing the negative effects of agglomeration. Providing NPs with a highly negative surface charge, far from the PZC at relevant pH values reduces interparticle attractive forces and prevents initial agglomeration, particularly in aqueous solution environments or for pre-soil application. Complementing electrostatic repulsion with steric forces can further improve NP stability, as evidenced by recent research pursuing highly tuned polymer chain lengths and zwitterionic molecules. Findings suggested that pairing active and inactive end groups can further stabilize NPs by fortifying the coating and inhibiting surface sorption. This can be accomplished using alternating positively and negatively charged end groups in the case of zwitterions, or by incorporating capped amine groups. Precoating NPs with a layer of large sterically repulsive biopolymers such as bacterial EPS or soil organic matter can create a natural protective layer that inhibits further adhesion or agglomeration. For some NPs that are less readily surface-modified, it may be possible to combine these methods to further enhance both antiagglomeration and bioactive delivery. Synthesis of a core-shell NP with a more stable inorganic coating further conjugated with an additional organic stabilizing coating could achieve both steric and electrostatic stabilization.

Emphasis on nontoxic, scalable, low-cost one-pot syntheses for effective coatings will be vital in achieving acceptance by the agricultural industry and consumers. The activity of coated NPs must be demonstrated beyond the lab and greenhouse to field studies, where a cost-to-benefit ratio can be weighed against traditional fertilizers and management strategies. The looming challenges of sustainable agriculture in the face of growing populations and climate variability will help find a receptive adoption of nanotechnology in agriculture.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2073-4395/10/7/1018/s1>.

Author Contributions: Conceptualization, D.W.B. and A.C.; methodology, A.C.; validation, D.W.B. and A.A.; formal analysis, A.C.; investigation, A.C., K.J., C.M.; resources, A.C., K.J., C.M.; data curation, A.C., K.J.; writing—original draft preparation, A.C.; writing—review and editing, D.W.B., A.A.; supervision, D.W.B.; project administration, D.W.B.; funding acquisition, D.W.B., A.A. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by USDA-NIFA, 2016-08771 and NSF-CBET, 1705874. Anthony Cartwright gratefully acknowledges support through the USU PDRF Program.

Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

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