Principles and practice of greener ionic liquid–nanoparticles biosystem

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S1. The role of ionic liquids in nanoparticles fabrication

Ionic liquids (ILs) can serve several roles in nanoparticles (NPs) fabrication, ensuring the desired morphology (size and shape) and limited agglomeration, which are crucial for nanobiotechnology applications.

S1.1. Stabilizing agent

(a) The stabilization of nanoparticles in ionic liquids based on intermolecular interactions:

The stabilization of NPs in ILs depends on intermolecular interactions.[S1] This stability is studied through the dual lens of physical and chemical considerations. Physical stability is evaluated at both macroscopic and microscopic scales, elucidating the ability of the colloidal system to maintain a singular phase and examining NP agglomeration in specific dispersion media.

In this hybrid IL-NP system, diverse intermolecular interactions are demonstrated, including van der Waals, electrostatic, structural, solvophobic, steric and hydrogen bonding forces. These interactions synergistically contribute to maintaining the stability of the NP dispersion in IL. The intricate interplay of these forces is susceptible to influences from internal and external factors that modulate the aforementioned interactions and consequently affect the stability of NPs in the IL milieu.[S2]

(b) The description of some examples of ILs that caused stabilization of NPs:

NPs are metastable systems that easily undergo physical and chemical transformations such as aggregation, size changes, or changes in chemical composition. Therefore, one of the key issues in preparation of NPs is the stabilization of newly synthesized products in terms of size-dependent properties. The interactions of NPs with biological systems depend on their dispersion, and structural, thermal and chemical stability (reactivity).[S3,S4] In this context, the

term "stability" is generally equated with dispersion stability. To assess the stability of nanodispersions, the zeta potential (ζ-potential) has been used as a measure of the surface electric charge of particles. High ζ-potential values (either negative or positive) indicate strong electrostatic repulsion between similarly charged NPs, which prevents their collision. In systems with low ζ-potential, electrostatic repulsion may be insufficient to overcome van der Waals attraction between NPs, which in turn can lead to their aggregation. Stable NPs are usually synthesized in the presence of capping/stabilizing agents (polymers, amphiphiles, and dendrimers, or disperse systems with nanosized domains such as microemulsions and micelles).[S3,S5]

ILs are effective stabilizers of nanodispersions. They may be applied alone or in combination with classical protective agents. ILs prevent aggregation or other unwanted structural changes of NPs by: (*i*) forming an electrical bilayer around NPs to provide electrostatic repulsion (electrostatic stabilization),[S6] (*ii*) forming a protective layer that acts as a steric barrier around NPs to physically prevent them from approaching each other (steric stabilization),[S1] or (*iii*) inhibiting NPs movement in the solution and decreasing agglomeration rate due to the relatively high viscosity of ILs.[S1,S7]

Redel et al.[S8] reported that 1-butyl-3-methylimidazolium tetrafluoroborate can self-assemble into an electrostatic sheath around AgNPs and positively influence their stability. NPs prepared without IL had a wide size distribution (10-100 nm) and precipitated within 1-2 h after reduction, whereas those obtained in the presence of IL were quite homogeneous in size (~10 nm) and remained stable for 3 days after synthesis. In another study,[S9] ether-functionalized IL (1-triethylene glycol monomethyl ether-3-methylimidazolium methanesulphonate) was found to provide steric stabilization for AuNPs. This occurred because the IL adsorbed onto the nanostructures in such a manner that the 1-triethylene glycol monomethyl ether tail extended away from the metal surface, increasing the distance between adjacent NPs. Apart from the mentioned mechanisms, more complex modes of action have been observed in the case of ILs functionalized with special ligands (e.g., nitrile, ether, thiol, amino, or carboxylic groups) that provide additional stabilization.[S7,S10] This stabilization can be observed in the case of 1-butyronitrile-3-methylimidazolium bis(trifluoromethanesulphonyl)imide (nitrile-functionalized IL), which is capable of stabilizing PdNPs and RuNPs through nitrile binding to the metal surface.[S11,S12]

(c) Factors that impact on stability of IL-NPs system

Endogenous and exogenous factors, such as the structure of ILs (including the alkyl chain length, anion type, functional group type, and quaternary core type), physicochemical

properties of both ILs and NPs, NP size and concentration, temperature, pressure, and water concentration, collectively influence the stability of NP dispersions in ILs by modulating the interactions involved.[S1,S7]

Among the diverse interactions, van der Waals, electrostatic, and steric interactions are well-established and quantifiable functions of the distance between adjacent NPs. Conversely, hydrogen bonding and structural forces are less extensively studied in a quantitative manner and are predominantly assessed qualitatively.[S13] Consequently, performing a quantitative comparison of the various interactions within an IL-NP hybrid system proves challenging. Most published reports on NP stability in ILs focus on one or two interactions, with limited consideration given to a combined assessment of these interactions aimed at maintaining NP stability in ILs.

Future research would benefit from exploring variables-such as NP size, temperature, solvent addition, and surface modification-that influence individual intermolecular interactions. In addition, the combined effects of interactions on the stability of NP dispersions in ILs should be investigated.

(d) Nanoparticle stability with ionic liquids: examples from current review

Quantitative information on stability in time of different ILs-NPs systems is presented in Table S1.

The stability in the presented systems varies widely, ranging from 7 days for the AuNPs system with ammonium IL with formate anion (case 5), to several weeks for AgNPs with pyridinium IL with trifluoroacetate anion (case 4) and for AgNPs with pyridinium IL with salicylate anion (case 8), and up to several months for all other examples.

Table S1 Stability of nanoparticles in the presence of ionic liquids

No	Type of NPs	Type of IL	Stability in time	Ref. number in line with main manuscript	Ref. number in line with SI
1	Pd	Imidazolium IL with bis(trifluoromethane-sulfonyl)imide anion	Several months	–	S12
2	Ag	Pyridinium IL with bromide anion	10 Months	23	S14
3	Au	Imidazolium IL with tryptophanate anion	4 Months	27	S15
4	Ag	Pyridinium Il with trifluoroacetate anion	3 Weeks	28	S16
5	Au	Ammonium IL with formate anion	7 Days	29	S17
6	Au	Imidazolium IL with acetate anion	4 Months	149	S18
7	Au	Ammonium IL with tryptophanate anion	Over 3 months	191	S19
8	Ag	Pyridinium IL with salicylate anion	2-4 Weeks	49	S20

## S1.2. Reducing (and also stabilizing) agent

To achieve reductive functionality of ILs, one can introduce certain functional groups (e.g., hydroxy) into their structure or use anions from formic or citric acid.[S10,S21,S22] Relatively few studies have been published on the application of ILs as reducing or reduction-promoting agents. For instance, trioctylmethylammonium citrate was used simultaneously as a reductor and protective agent for the preparation of Ag and Au NPs from silver nitrate and chloroauric acid, respectively.[S22] However, IL-mediated reduction may not always follow a simple redox mechanism, e.g., by the decomposition of Ru precursor complexes by 1-hexyl-2,3-dimethylimidazolium bis(trifluoromethane)sulphonimide and subsequent reduction of the products to yield RuNPs.[S10,S21,S22]

Another interesting example is the use of biodegradable protic IL as a reducer and a capping agent for AgNPs,[S23] whose stabilization mechanism is shown in Fig. S1a. The mechanism of electrostatic interaction between protic ILs represented by ammonium ILs with anions represented by selected phenolic acids: gallic, caffeic, and *p*-coumaric and AgNPs was

confirmed based on the analysis of characteristic bands in FT-IR spectra, Raman spectra, and microscopic studies using TEM. Based on the observation of a significant change in the position of the absorption band attributed to the stretching vibrations of hydroxyl groups in FT-IR spectra taken separately for IL and IL-AgNPs, the responsibility of the hydroxyl groups of phenolic acids for the interaction between IL and the AgNPs surface was confirmed. As a result, it was found that the reduction of Ag^+ ions to AgNPs probably occurs simultaneously with the formation of specific quinones, which are then adsorbed on the surface of the NPs. Additionally, Raman analysis allowed to the observation of high intensities of peaks assigned to the aromatic ring compared to those belonging to the other structural elements of the ILs structure. This allowed to conclude that during the interaction of NPs with IL, its cation and the remaining part of the anion are probably located further away from the surface of the AgNPs than the aromatic ring of the anion of IL. Microscopic tests confirmed the protective behaviour of the IL, which forms a film on the surface of the NPs, ensuring their high stability and protection against agglomeration. Another interesting example is the image of the static stabilization of AuNPs by imidazolium ILs with tryptophanate anion, enriched with an alkyl chain of different length (C2 or C12) in the cationic structure. This stabilization mechanism is shown in Fig. S1c. It was found that selected ILs can act as both a reducing agent and a capping reagent. Higher stability and dispersibility of AuNPs, and thus a reduced tendency to agglomerate were obtained in the case of IL containing a longer alkyl chain in the cation. According to the authors, this could be a kind of evidence that the IL cation is involved in ensuring the proper distance between neighboring AuNPs and therefore must be located at a greater distance from the NPs surface. Therefore, the IL anion must probably has to interact directly with the surface of AuNPs generated as a result of reduction, which, according to literature reports, is related to the oxidation of the indole moiety of tryptophan to the oxindole form. The stabilization of AuNPs is ensured by the formation of a protective network of ILs molecules around their surface. Reducing and stabilizing properties of IL in the synthesis of AgNPs have also been demonstrated for imidazolium IL with a metronidazole core in the cation and containing a naturally occurring citrate anion in the structure.[S24] The course of the synthesis of the IL and its role in the synthesis of AgNPs is presented in Fig. S2. Changes in the position of the adsorption bands corresponding to specific functional groups of IL observed after the synthesis of AgNPs confirmed the occurrence of interactions taking place on the surface of the NPs with the citrate anion of IL, and the expanded metronidazole cation was directed outwards. This was confirmed, together with TGA tests, by the formation of a protective organic layer by the IL with an average amount of more than 2%.
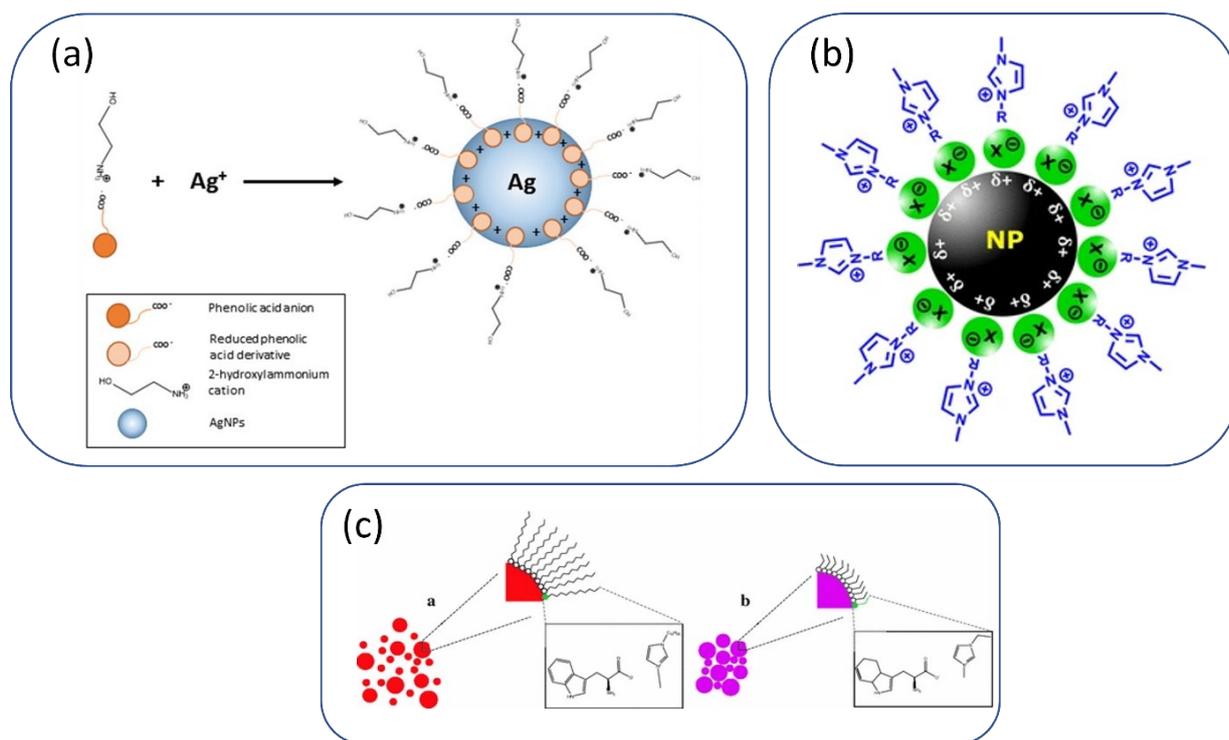
Fig. S1. Schematic representation of mechanisms of: a) electrostatic stabilization of AgNPs by ammonium ILs, b) electrostatic stabilization of NPs by imidazolium IL and c) static stabilization of AuNPs by imidazolium ILs. a) Reproduced with permission.[S23] Copyright 2017, Elsevier. b) Reproduced with permission.[S25] Copyright 2016, Springer. c) Reproduced with permission.[S15] Copyright 2011, Springer.
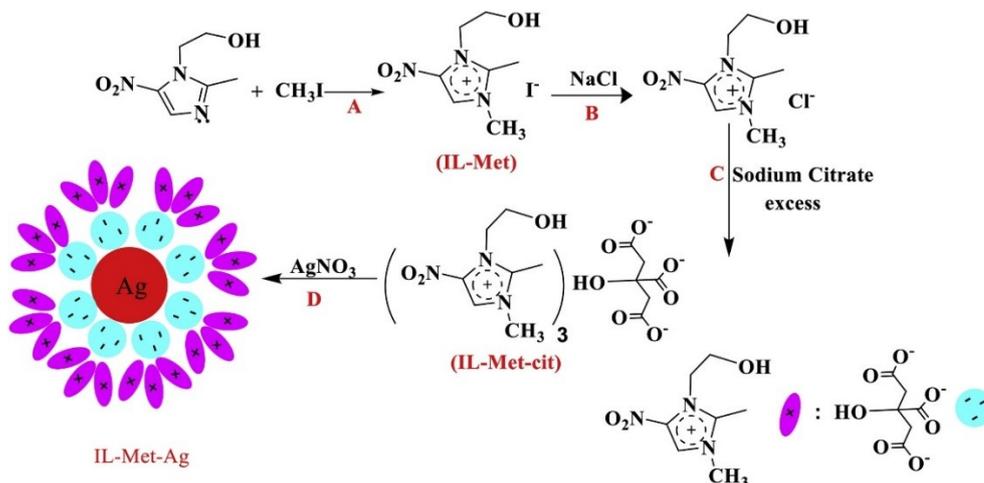
Fig. S2. Synthetic processes of AgNPs: preparation of IL-Met-cit and reaction with silver nitrate. Reproduced with permission.[S24] Copyright 2020, Elsevier.

S1.3. Metal precursor

ILs that contain a metal in the structure as an anion (tetrachloroaurate, tetrachlorocuprate(II)) or as a cation (zinc alkylamine complexes) can play the role of initial materials for the fabrication of NPs under reductive conditions. The careful selection of IL

components influences the morphology of the resulting NPs.[S7] Residual ligands of the IL can also serve as stabilizing agents for produced NPs and prevent their aggregation.[S26] For example, it is possible to prepare well-dispersed AgNPs (5.7 to 8.3 nm) while nitrate(V) IL with [bis(alkylethylenediamine) silver(I)] cation is treated with a reducing agent (NaBH$_4$).[S27]

S1.4. Reaction media

An advantage of ILs is that they regulate the solubility of reactants as well as the mass and heat transfer in the system along with the growth of NPs and the NPs' properties.[S1,S10] Due to their low vapor pressure and high boiling point, it is possible to carry out reactions with ILs at high temperature and pressure. They also have the ability to absorb microwave (MW) radiation due to the high polarizability and ionic structure of ILs, which increases the rate of the formation of small-diameter NPs caused by rapid heating.

ILs control the solubility of reactants, the mass and heat transfer in the system, the degree of NPs stabilization, and the product properties.[S1,S10] Different ILs have been shown to provide dissimilar structural cues for growing nanostructures. To date, the use of ILs has allowed the production of a variety of morphologies, such as ZnO nanosheets,[S28] Bi$_2$S$_3$ nanowires (arranged in flower-like structures),[S29] or α-FeOOH hollow spheres.[S30] Research on the relationship between the molecular structure of ILs and the properties of NPs has focused on imidazolium ILs because they are the most commonly used systems for the fabrication of NMs. In most cases, the increase in the length of the alkyl chain in the cation is accompanied by a decrease in the diameter of the NPs, although this rule is not absolute.

The coordination ability of the anion is also important. The use of more coordinated anions (e.g., hexafluorophosphate or ethylsulphate) leads to finer NPs relative to less coordinated anions (e.g., bis(trifluoromethanesulphonyl)imide).[S1,S10] As an example, a preparation of IrNPs in the presence of 1-butyl-3-methylimidazolium[S31] yields nanostructures with an average size of 2.9 nm for tetrafluoroborate anion, 2.6 nm for trifluoromethane sulphonate, and 2.4 nm for hexafluorophosphate, i.e., the most coordinated. Similar results were reported for Ru[S32] and Pt NPs.[S33,S34]

Regardless of the choice of an IL, the influence of additional factors on the characteristics of the products remains significant (temperature, concentration of precursor, and type of stabilizers). For example, nanosized SiO$_2$ prepared in IL-containing microemulsions can have different shapes depending on the pH of the reaction system (empty spheres in alkaline conditions and ellipsoids at acidic pH).[S35] In turn, the growth of CuO nuclei prepared via MW-assisted methods in the presence of 3-methyl-1-octylimidazolium trifluoroacetate was shown

to be temperature-dependent. The synthesis at 80°C resulted in leaf-shaped NPs, whereas nanoneedles were obtained at 100°C.[S36]

The use of ILs as a reaction media for the synthesis of NMs is not without drawbacks. One of the most common problems is insufficient solubility of certain reagents (typically metal precursors) in an IL. Strategies that address this issue include the introduction of co-solvents (polyethylene glycol, water and hexane) or stabilizers (e.g., cetrimonium bromide – CTAB, oleic acid) to the reaction mixture, functionalization of IL cation, temperature increases, or the use of IL-containing microemulsions as reaction systems.[S7,S10]

S1.5. Functionalizing agent

The properties of freshly synthesized NPs may be enhanced or modified by their surface functionalization with suitable agents (usually polymers). The functionalizing effect of ILs is achieved through their physical absorption or covalent anchoring to the nanostructure surface through the functional groups present in the liquid structure (amine, thiol, and carboxyl groups). Chemical bonding affects the properties of ILs (such as the melting point) and the stability and solubility of the synthesized NPs.[S1,S37] Therefore, it is possible to obtain novel hybrid materials that combine the features of both NPs and ILs, e.g., by immobilizing functionalized ILs on magnetic NPs as recyclable catalysts.[S1,S37]

S1.6. Template

ILs offer additional in situ stabilization of growing NPs. They can control NP morphology or size through a templating function.[S21,S38] The relationship between the structural properties of the cation and anion, and the size of the resulting NPs play an important role. The increase in the length of the alkyl chain in the imidazolium cation often favors the formation of smaller NPs. The same rule has been applied with increasing anion-coordinating abilities.[1,10] For instance, 1-butyl-3-methylimidazolium chloride was found to alter the shape and size of ZnONPs synthesized via an ultrasound-assisted route.[S39] The application of IL as a medium led to the formation of well-defined spheres (with a mean diameter of 24 nm) rather than irregular plate-like nanostructures.

S2. Scale of the processes of ILs-NPs systems syntheses

The scale of the syntheses described is the main manuscript is given in Table S2. As it can be seen, all of the examples presented were on laboratory scale. The amount of a NPs precursor was between 0.05 mg[S40] and 3.4 g[S41] and between 0.25 Ml[S40] or 0.4 mg[S16] and 1000 mg[S20] or 30 Ml[S42] for an IL. Since none of the examples described mention a process scale larger than a laboratory scale, the issue of scaling up the ILs-NPs synthesis process, as described in section 3.1, becomes even more important in the case of its real-world implementation.

Table S2. Amounts of metal reagents (metal nanoparticles' precursor and ionic liquid) used in the examples presented in the manuscript in Tables 5, 6 and 7. The references here are consistent with those for the main manuscript.

No	Amount of a metal precursor[a]	Amount of an IL[a]	Ref. number in line with main manuscript	Ref. number in line with SI
1	170 mg	100 mg	23	S14
2	0.34 mg	5.0 mL	27	S15
3	0.34 mg	0.4 mg	28	S16
4	2.6 – 17.0 mg	50 mg	29	S17
5	0.18 mg	2 g	149	S18
6	3.4 mg	9.22 or 6.65 mg	191	S19
7	0.17 – 1.7 mg	5.0 – 1000 mg	49	S20
8	34 mg	20 mL	47	S24
9	0.05 mg	0.25 mL	150	S40
10	3.4 g	1.47 – 2.36 mg	136	S41
11	0.22 g	30 mL	40	S42
12	16 mg	3.0 mL	16	S43
13	9.3 mg	33.4 mg	18	S44
14	1.70 mg	3.0 – 3.5 mg	22	S45
15	1.70 mg	35 mg	30	S46
16	–	1.0 mL	31	S47
17	–	1.0 mL	32	S48
18	–	1.0 mL	33	S49
19	256 mg	160 – 320 mg	34	S50
20	1.70 g	–	35	S51
21	1.70 mg	–	36	S52
22	–	–	37	S53
23	–	1.0 mL	38	S54
24	–	1.0 mL	39	S55
25	1.98 g	–	46	S56

26	0.6 mg	1.0 mL	130	S57
27	0.42 g	30 mL	48	S58
28	–	1.0 mL	133	S59
29	–	1.0 mL	134	S60
30	12 mg	2.0 mL	132	S61
31	3.0 mg	0.3 mL	135	S62
32	1.7 mg	50 mg	138	S63
33	1.7 mg	35.2 – 47.4 mg	152	S64
34	1.7 mg	35.6 mg	153	S65
35	1.7 mg	35.6 mg	154	S66
36	1.7 mg	35.2 – 47.4 mg	155	S67
37	–	3.0 mL	157	S68
38	100 mg	100 mg	161	S69
39	0.2 g	2.0 mL	162	S70
40	5.0 mg	1.0 mL	168	S71
41	1.9 mg	–	207	S72
42	–	1.0 mL	208	S73
43	–	1.0 mL	209	S74
44	–	1.0 mL	210	S75
45	–	1.0 mL	211	S76
46	–	1.0 mL	212	S77

[a]In case of no value given (indicated as '–'), the amount of either a NPs' precursor or an IL was not clear from the article.

S3. Nanoparticles characteristic in terms of physicochemical properties of ionic liquids

The physicochemical properties of ILs, including but not limited to melting and decomposition temperatures, polarity, density, transport properties, surface and interfacial tensions, and surface activity, exert a significant influence on the size, morphology, and other properties of NPs.[S7]

In particular, the coordination ability of the IL anion correlates with the smaller average diameters observed in metal NPs.[S78] The effect of the alkyl chain length in the IL cation, along with the size of non-polar nanodomains within the supramolecular structure, on particle size depends on the ionic or nonionic nature of the precursor.[S79] Further elucidation on the control of NP size and shape through the use of ILs is provided in the following section.

Due to their amphiphilic structure and inherent charge, ILs play a prominent role in protecting NPs by mitigating electrostatic repulsion through both charge and steric stabilization mechanisms.

Transport properties, which include viscosity, diffusion coefficient, electrical conductivity, and thermal conductivity, are critical parameters in the design and advancement of NP preparation methods.[S80] These properties have a significant impact on chemical processes involving ILs, not only when they are used as reaction media, but also when they serve as reagents or additives.

The higher viscosity of ILs induces a reduction in the aggregation rate of colloidal NPs, which is different from the behavior observed in water or conventional organic solvents.[S7] The viscosity values inherent to ILs are mainly determined by their ability to engage in van der Waals interactions and hydrogen bonding. While higher viscosity affects the diffusion of reagents within ILs, it also limits the electrical and thermal conductivity of ILs. This limitation extends to mass and heat transfer during NP synthesis.[S80,S81]

Surface and interfacial tensions play a key role, and it is a common observation ILs typically exhibit lower surface tensions than water at room temperature. This reduction in surface tension is advantageous as it can contribute to increased nucleation rates, mitigate Ostwald ripening, and consequently promote the formation of smaller NPs.[S82]

The amphiphilic nature of ILs endows them with surface activity that allows the formation of organized structures within nanosolutions, such as micelles, vesicles, lyotropic liquid crystals, gels, and microemulsions.[S7] This inherent surface activity further enhances the versatility of ILs in nanotechnology, providing avenues for controlled assembly and design of nanostructures.

S3.1. Size and shape control of nanoparticles in terms of physicochemical properties of ionic liquids

Any factors affecting the stability of NPs in ILs has the potential to induce changes in NP size[S83,S84] and/or morphology[S85,S86] during the synthesis process. The size and size distribution of NPs synthesized in ILs are strongly influenced by the physicochemical properties of ILs, thereby affecting NP stabilization.[S1] For example, ILs characterized by longer side chains result in smaller diameters and narrower distributions in the synthesized nickel and ZnO NPs. This phenomenon is attributed to the significant influence of longer side chains on NP stability within ILs, which exerts modifications on the physicochemical properties of IL and the interactions between ILs and NPs.[S87,S88]

The presence of larger sizes or different morphologies in synthesized NPs can result from the agglomeration of unstable primary NPs. This agglomeration can be induced by factors such as smaller IL anions that exhibit enhanced cation-anion Coulomb attraction[S89] or less coordinating anions within ILs.[S86] In addition, higher temperatures contribute to reduced IL viscosity and increased diffusion velocities of sputtered NPs.[S90,S91] Thus, a more nuanced understanding of the stability of NP dispersions in ILs is of considerable importance in advancing efforts to synthesize NPs of precisely controlled size and morphology in this medium.

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