

*Short Review*

## **Inorganic materials synthesis in ionic liquids**

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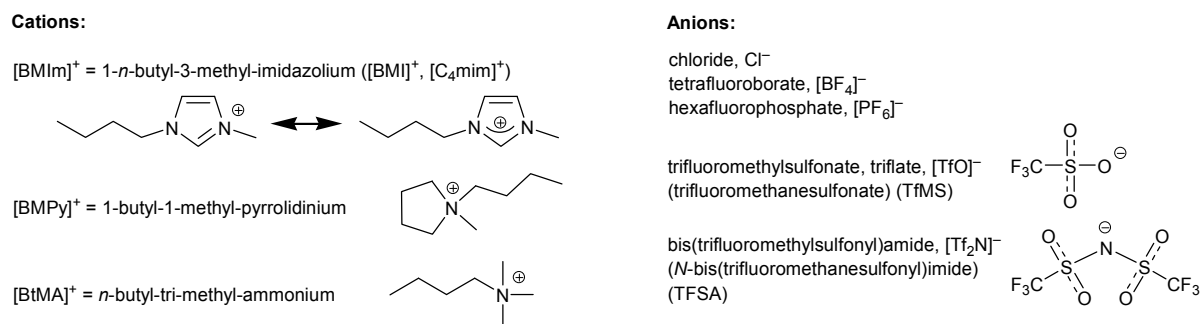
**Abstract:** The field of "inorganic materials from ionic liquids" (ILs) is a young and dynamically growing research area for less than 10 years. The ionothermal synthesis in ILs is often connected with the preparation of nanomaterials, the use of microwave heating and in part also ultrasound. Inorganic material synthesis in ILs allows obtaining phases which are not accessible in conventional organic or aqueous solvents or with standard methods of solid-state chemistry or under such mild conditions. Cases at hand include "ligand-free" metal nanoparticles without added stabilizing capping ligands, inorganic or inorganic-organic hybrid solid-state compounds, large polyhedral clusters and exfoliated graphene from low-temperature synthesis. There are great expectations that ILs open routes towards new, possibly unknown, inorganic materials with advantageous properties that cannot (or only with great difficulty) be made via conventional processes.

**Keywords:** inorganic materials; ionothermal synthesis; ionic liquids; microwaves

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### **1. Ionic liquids**

By definition ionic liquids are salts with a melting point below 100 °C. Many ILs are liquid at room temperature (RT-ILs). The liquid state is favored by conformationally flexible and weakly coordinating ions with small lattice enthalpies [1]. Examples of IL cations and anions are shown in Figure 1. ILs have a high thermal stability, high charge density, polarity, dielectric constant, ionic conductivity, a wide liquid-state temperature range, a very low vapor pressure and the ability to dissolve a variety of materials. Ionic liquids have become interesting alternatives to traditional aqueous or organic solvents and are intensively investigated as new liquid media for synthesis and catalysis [2-14]. The promising preparation of advanced functional materials which use ILs is also called "ionothermal synthesis" [15]. The role of ILs in ionothermal synthesis can be templating, co-templating and no templating so that ILs may also offer morphology control of materials [15].

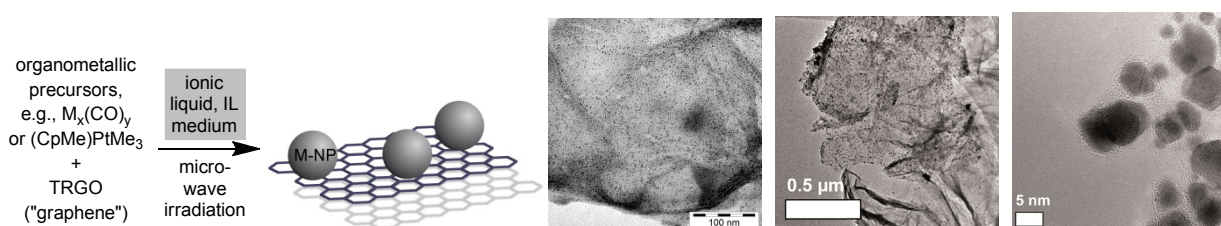


**Figure 1. Common cations and anions of non-functionalized ILs.**

## 2. Materials from ionothermal synthesis

Ionic liquids have been used as media, e.g., for the syntheses of zeolites, inorganic-organic hybrid materials and frameworks such as metal-organic frameworks (MOFs) [16,17], clathrates [18], metal nanoparticles also as deposits on support materials [19], metal oxides including ZnO [20] or CuO semiconductor nanoparticles [21,22], metal chalcogenides [23,24], polynuclear metal complexes [25-27], micro-/mesoporous carbon and graphene from graphite exfoliation [28] etc.

The synthesis of metal nanoparticles (M-NPs) in ionic liquids (ILs) can start from metals, metal salts, metal complexes and in particular metal carbonyls and can be carried out by chemical reduction, thermolysis, photochemical, microwave irradiation, ultrasound induced decomposition, electroreduction or gas phase synthesis, including sputtering, plasma/glow-discharge electrolysis, physical vapor deposition or electron beam and  $\gamma$ -irradiation [19,29]. Metal carbonyls, M<sub>x</sub>(CO)<sub>y</sub> are commercially available and elegant precursors because the metal atoms are already in the zero-valent oxidation state for M-NPs so that no reduction is necessary. From the IL dispersion the M-NPs can be deposited on various surfaces, including carbon derivatives like "graphene" (Figure 2) [19,30,31].



**Figure 2. Microwave-induced organometallic precursor decomposition in the presence of thermally reduced graphite oxide (TRGO) in ILs to give, e.g., RuNP@TRGO (left TEM) and PtNP@TRGO (middle and right TEM). The IL also exfoliates the TRGO sheets [31,32].**

## 3. Why microwaves for ionothermal synthesis?

Ionic liquids have significant absorption efficiency for microwave energy because of their high ionic charge, polarity and dielectric constant and, thus, are attractive media for microwave reactions.

Microwave heating is extremely rapid. Microwave radiation can interact directly with the reaction components, so they heat the reaction mixture and not the vessel. The reactant mixture absorbs the microwave energy and localized superheating results in fast and efficient heating times with temperatures of 200 °C reached within seconds. The use of microwaves is a rapid way to heat reactants compared with conventional thermal heating. Microwaves are also an "instant on/instant off" energy source which reduces the risk when heating reactions [33-37].

## References

1. Weingärtner H, (2010) Understanding ionic liquids at the molecular level: Facts, problems, and controversies. *Angew Chem Int Ed* 47: 654-670.
2. Welton T, (1999) Room-temperature ionic liquids. Solvents for synthesis and catalysis. *Chem Rev* 99: 2071-2084.
3. Taubert A, Li Z, (2007) Inorganic materials from ionic liquids. *Dalton Trans* 723-727.
4. Wasserscheid P, Keim W, (2000) Ionic liquids – new "solutions" for transition metal catalysis. *Angew. Chem. Int. Ed.* 39: 3772-3789.
5. Pârvulescu VI, Hardacre C, (2007) Catalysis in ionic liquids. *Chem Rev* 107: 2615-2665.
6. Lodge P, (2008) A unique platform for materials design. *Science* 321: 50-51.
7. Plechkova NV, Seddon KR, (2008) Applications of ionic liquids in the chemical industry. *Chem Soc Rev* 37: 123-150.
8. Torimoto T, Tsuda T, Okazaki K et al. (2010) New frontiers in materials science opened by ionic liquids. *Adv Mater* 22: 1196-1221.
9. Hallett JP, Welton T, (2011) Room-temperature ionic liquids: Solvents for synthesis and catalysis. 2. *Chem Rev* 111: 3508-3576.
10. Ahmed E, Breternitz J, Groh MF, et al. (2012) Ionic liquids as crystallization media for inorganic materials. *CrystEngComm* 14: 4874-4885.
11. Carriazo D, Concepción Serrano M, Concepción Gutiérrez M et al. (2012) Deep-eutectic solvents playing multiple roles in the synthesis of polymers and related materials. *Chem Soc Rev* 41: 4996-5014.
12. Scholten JD, Leal BC, Dupont J, (2012) Transition metal nanoparticle catalysis in ionic liquids. *ACS Catalysis* 2: 184-200.
13. Feldmann C, (2013) Ionic liquids in chemical synthesis – progress and advantages as compared to conventional solvents. *Z Naturforsch* 68b: 1057-1057.
14. Groh MF, Müller U, Ahmed E, et al. (2013) Substitution of conventional high-temperature syntheses of inorganic compounds by near-room-temperature syntheses in ionic liquids. *Z Naturforsch* 68b: 1108-1122.
15. Morris RE, (2009) Ionothermal synthesis – ionic liquids as functional solvents in the preparation of crystalline materials. *Chem Commun* 2990–2998.
16. Morris RE, (2010) Ionothermal synthesis of zeolites and other porous materials, In: Cejka J, Corma A, Zones S Editors, *From Zeolites and Catalysis*, Vol. 1, Weinheim: Wiley-VCH, 87-105.
17. Parnham ER, Morris RE, (2007) Ionothermal synthesis of zeolites, metal-organic frameworks and inorganic-organic hybrids. *Acc Chem Res* 40: 1005-1013.
18. Guloy AM, Ramlau R, Tang Z, et al. (2006) A guest-free germanium clathrate. *Nature* 443: 320-323.

19. Janiak C, (2013) Ionic liquids for the synthesis and stabilization of metal nanoparticles. *Z Naturforsch* 68b, 1059-1089.
20. Zou H, Luan Y, Ge J, et al. (2011) Synthesis of ZnO particles on zinc foil in ionic-liquid precursors. *CrystEngComm* 13: 2656-2660
21. Taubert A, Stange F, Li Z, et al. (2012) CuO nanoparticles from the strongly hydrated ionic liquid precursor (ILP) tetrabutylammonium hydroxide. *ACS Appl Mater Interfaces* 2012, 4, 791-795.
22. Alammar T, Birkner A, Mudring A-V, (2009) Ultrasound-assisted synthesis of CuO nanorods in a neat room-temperature ionic liquid. *Eur J Inorg Chem* 2765-2768.
23. Rodríguez-Cabo B, Rodil E, Rodríguez H, et al. (2012) Direct preparation of sulfide semiconductor nanoparticles from the corresponding bulk powders in an ionic liquid. *Angew Chem Int Ed* 51: 1424-1427.
24. Lin Y, Dehnen S, (2011) [BMIm]<sub>4</sub>[Sn<sub>9</sub>Se<sub>20</sub>]: Ionothermal synthesis of a selenidostannate with a 3D open-framework structure. *Inorg Chem* 50: 7913-7915.
25. Lin Y, Massa W, Dehnen S, (2012) "Zeoball" [Sn<sub>36</sub>Ge<sub>24</sub>Se<sub>132</sub>]<sup>24-</sup>: A molecular anion with zeolite-related composition and spherical shape. *J Am Chem Soc* 134: 4497-4500.
26. Ahmed E, Ruck M, (2011) Chemistry of polynuclear transition-metal complexes in ionic liquids. *Dalton Trans* 40: 9347-9357.
27. Xiong W-W, Li J-R, Hu B, et al. (2012) Largest discrete supertetrahedral clusters synthesized in ionic liquids. *Chem Sci* 3: 1200-1204.
28. Cai M, Thorpe D, Adamson DH, et al. (2012) Methods of graphite exfoliation. *J Mater Chem* 22:24992-25002.
29. Dupont J, Scholten JD, (2010) On the structural and surface properties of transition-metal nanoparticles in ionic liquids. *Chem Soc Rev* 39: 1780-1804.
30. Vollmer C, Janiak C, (2011) Naked metal nanoparticles from metal carbonyls in ionic liquids: Easy synthesis and stabilization. *Coord Chem Rev* 255: 2039-2057.
31. Marquardt D, Vollmer C, Thomann R, et al. (2011) The use of microwave irradiation for the easy synthesis of graphene-supported transition metal hybrid nanoparticles in ionic liquids. *Carbon* 49: 1326-1332.
32. Marquardt D, Beckert F, Pennetreau F, et al. (2014) Hybrid materials of platinum nanoparticles and thiol-functionalized graphene derivatives. *Carbon* 66: 285-294.
33. Mingos DMP, Baghurst DR, (1991) Applications of microwave dielectric heating effects to synthetic problems in chemistry. *Chem Soc Rev* 20: 1-47.
34. Galema SA, (1997) Microwave chemistry. *Chem Soc Rev* 26: 233-238.
35. Larhed M, Moberg C, Hallberg A, (2002) Microwave-accelerated homogeneous catalysis in organic chemistry. *Acc Chem Res* 35: 717-727.
36. Bilecka I, Niederberger M, (2010) Microwave chemistry for inorganic nanomaterials synthesis. *Nanoscale* 2: 1358-1374.
37. Leonelli C, Mason, TJ, (2010) Microwave and ultrasonic processing: Now a realistic option for industry. *Chem. Engineering and Processing* 49: 885-900.

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