# Counterion-mediated growth of ruthenium nanoparticles stabilised by polymerized ionic liquids for future catalysis applications

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Ruthenium nanoparticles (RuNPs) have garnered significant interest as catalysts for many industrially important reactions, but in order to attain commercial viability, their catalytic activity and selectivity, stability, and recyclability must be improved. These RuNPs can be stabilised through the addition of polymerised ionic liquids (PILs) during synthesis, which sterically and electrostatically stabilise the RuNPs while maintaining chemical accessibility to the catalyst surface. Preliminary investigations with in-house SAXS have shown that the size dispersion of RuNPs stabilised by imidazolium-based cationic PILs, *i.e.* Ru@PIL(+), vary dependent on the PIL counterion, with previously published X-ray photo-correlation spectroscopy (XPS) data from our consortium suggesting that this may be due to whether the counterion or the PIL chain interacts with the RuNP surface. [1,2] Using small-angle X-ray and neutron scattering (SAXS/SANS), transmission electron miscoscopy (TEM) we have revealed that the PIL counterion was the key parameter towards tuning the morphologies of Ru@PIL(+) during synthesis in ethylene glycol, while the pendant alkyl chain group length had only a minor influence. We propose a mechanism whereby the PIL mesh size dictates the size of the RuNP formed, then the size of the counterion and its affinity with the RuNP surface controls the aggregation of these particles through "electrosteric" stabilisation ( **Figure 1** ). In the case of each counterion: with **Cl** $^-$ , spherical RuNPs were obtained, whose radius was directly related to the PIL concentration (and thus mesh size), ranging between 0.7 and 1.5 nm; with **Br** $^-$ , 1 nm spherical RuNPs coexist with 3 nm cluster forms and further aggregated mass fractals, irrespective of the PIL concentration; while for **I** $^-$ , solely larger objects were obtained. These structures were preserved when redispersed in water, and their behaviour in complexed polyelectrolyte coacervate gels containing high concentrations of RuNPs was also studied as a promising reaction medium. These insights, combined with data on catalytic performance, will produce essential links between RuNP nanomorphologies and catalytic activity.

**Keywords:**
Metallic nanoparticles, nanocatalysis, polymers, stabilizers, aggregation behaviour, coacervates

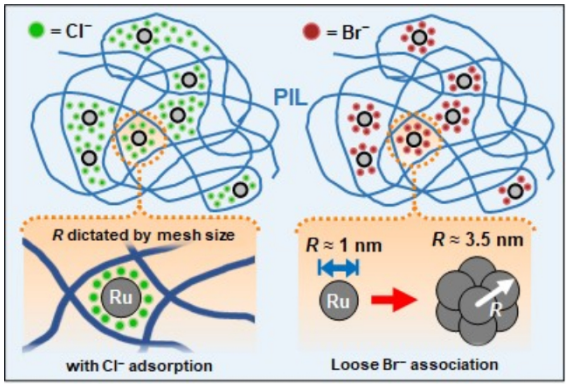


*Figure 1. Schematic illustrating the proposed mechanism by which RuNPs grow in synthesis when stabilised by imidazolium-based polymerised ionic liquids and their associated counteroins. These RuNP structures are then replicated when the products are purified and redispersed in water.*

**References:**

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