Novel one pot synthesis of silver nanoparticle–polymer composites by supercritical CO_2 polymerisation in the presence of a RAFT agent†

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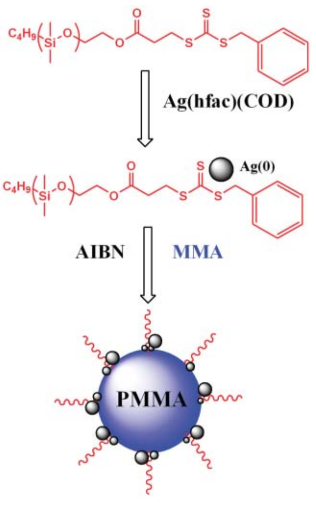
We report the one pot synthesis of a silver–polymer nanocomposite in supercritical carbon dioxide ($scCO_2$) whereby an organometallic silver complex is thermally decomposed in the presence of a reversible addition fragmentation chain transfer (RAFT) agent during a polymerisation reaction in which the RAFT agent simultaneously stabilises the growing polymer microparticles and the formation of surface located silver nanoparticles.

Metal nanoparticles have been the subject of extensive interest because of their unique size dependent functional properties which lead to various catalytic, optoelectronic and biomedical applications.[1] Silver nanoparticles in particular have antimicrobial properties[2] and excellent potential as biosensing materials for surface enhanced Raman scattering (SERS) and metal enhanced fluorescence.[3] The embedding of these nanoparticles into a polymer substrate is an ideal way to support and protect the nanoparticles whilst stabilising them against aggregation and facilitating ease of application and simple recovery.

Here we report the synthesis of a silver nanoparticle–polymer composite material in the absence of any conventional solvents. The synthesis is performed in supercritical carbon dioxide ($scCO_2$) in a single pot, single step reaction. The absence of conventional organic solvents is preferential as it avoids the possibility of solvent residues, which would be disadvantageous for medical or biodetection applications. In addition, $scCO_2$ is seen as a green alternative to conventional solvents, it is non-toxic and can be simply removed without leaving any residues in the material.[4]

RAFT polymerisation is a facile technique for the functionalisation of polymer chain ends that can produce narrow polydispersity products. RAFT polymerisation reactions have been recently performed in $scCO_2$[5] and the technique has also been successfully applied to dispersion polymerisation.[6] Silver nanoparticles have also been synthesised in $scCO_2$ through the use of $scCO_2$ soluble precursors and stabilising agents.[7] Here, we demonstrate that a $scCO_2$ soluble RAFT agent can be designed to fulfil two roles in a single reaction: polymerisation and stabilisation of polymer as well as stabilisation of silver nanoparticles. The RAFT agent is used as a non-migratory surfactant; it effectively grafts into the growing polymer particle by RAFT chemistry, while the CO_2-philic Z-group (Scheme 1) acts as a polymeric stabiliser. Therefore, the RAFT moiety will always be located at the surface of the polymer particle. The RAFT agent also acts simultaneously to stabilise the formation of silver nanoparticles through favourable silver–sulfur interaction.[8] Because the silver nanoparticles are attached to the RAFT agent, this directs the silver nanoparticles to the surface of the polymer where they are advantageously positioned for most applications.

The RAFT agent utilised in this work (Scheme 1) is formed from the combination of polydimethylsiloxane (PDMS) and benzylsulfanylthiocarbonylsulfanylpropionic (BSTSP) acid to form a PDMS-RAFT agent (see ESI† for synthesis). Because of its affinity for CO_2, the PDMS moiety will position the RAFT agent on the surface of the growing polymer, as well as ensuring effective stability of the growing polymer particle. The electron rich sulfur groups of the BSTSP acid moiety are attracted to the electron deficient surface of the forming silver nanoparticles, providing *in situ* stabilisation. It should be noted that we are not using RAFT as a polymerisation controlling agent, but merely as a means to provide surface functionalisation of the polymer particle. Indeed, it is well known that trithiocarbonates of the form used in this report are poor mediating agents for methyl methacrylate (MMA) polymerisations. We are currently designing new macro-RAFT agents that will additionally control the polymer molecular weight.



Scheme 1 Schematic diagram showing the process of silver-nanocomposite formation. The nanoparticles are stabilised by interaction with the sulfur groups on the RAFT agent while the polymer microparticle is formed by dispersion polymerisation of MMA in $scCO_2$ stabilised by the simultaneous grafting of a CO_2-philic macro-RAFT agent.

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† Electronic supplementary information (ESI) available: Synthesis details of RAFT agent, GPC, NMR, EDX data and additional TEM images. See DOI: 10.1039/b710503g

Silver nanoparticle synthesis and polymer synthesis reactions were first performed separately to ensure both worked successfully in the presence of RAFT stabiliser. Polymer microparticles were formed by adding 500 mg PDMS-RAFT and 60 mg azobisisobutyronitrile [AIBN, 0.6 wt%] to the autoclave and flushing with CO_2 for 15 minutes. Degassed MMA (10 ml) was then added under a slightly positive flow of CO_2 in order to prevent the ingress of oxygen into the system. The autoclave was pressurised to 55 bar, heated to 65 °C and then pressurised to 275 bar. After 48 h, the vessel was cooled to room temperature and the CO_2 vented. The resulting polymer was a free-flowing, off-white powder. SEM investigation of this powder (Fig. 1b) shows discrete spherical particles of $\sim$1–4 μm.

The synthesis of silver nanoparticles was performed by loading 100 mg of (1,5-cyclooctadiene)(hexafluoroacetylacetonate)silver(I) [Ag(hfac)(COD)] into an autoclave with 300 mg PDMS-RAFT. The autoclave was then flushed with CO_2 for 15 min before being heated to 65 °C and pressurised to 275 bar $scCO_2$. The reaction was maintained at these conditions for 48 h before being cooled to room temperature and depressurised. Chloroform (10 ml) was then added as solvent to disperse and remove PDMS-RAFT stabilised silver nanoparticles as a transparent brown solution. Chloroform was chosen as the dispersing medium because of the very high solubility of PDMS in this solvent. TEM investigation of this solution (Fig. 1a) showed silver nanoparticles mostly of 5–20 nm in size. Brown colouration is characteristic of the plasmon resonance absorption of silver nanoparticles. The Ag(hfac)(COD) and PDMS-RAFT used in the synthesis of these nanoparticles are both readily $scCO_2$ soluble. The Ag(hfac)(COD) acts as the silver feedstock as it is thermally decomposed during the reaction to yield elemental silver. As the silver nanoparticles are formed, they are stabilised by the PDMS-RAFT that is dissolved in the $scCO_2$. As the TEM micrographs show little agglomeration of the nanoparticles, it can be assumed that this stabilisation is very effective.

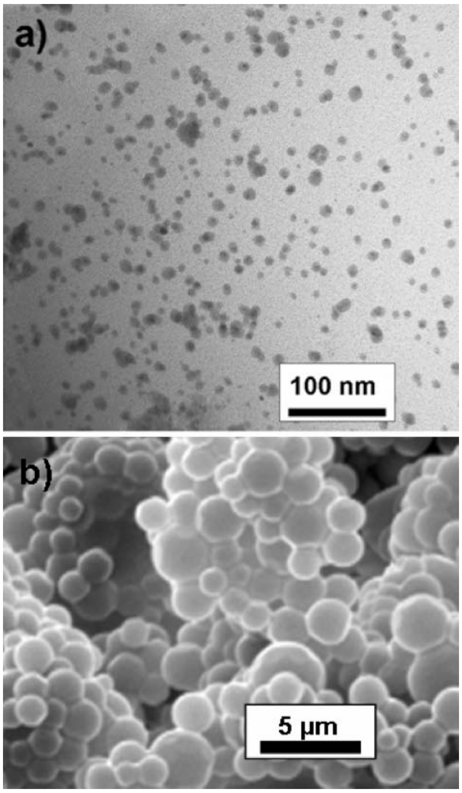

Fig. 1 a) Bright field TEM image of silver nanoparticles synthesised in the absence of polymer. b) Secondary electron SEM image of polymer powder synthesised in the absence of silver.

The one pot, simultaneous reaction was performed under identical conditions to the polymer synthesis except that 200 mg Ag(hfac)COD were added to the autoclave along with the other reactants. The reaction resulted in the production of a fine free-flowing brown powder. TEM and SEM images of this product are shown (Fig. 2a and 2b respectively). SEM investigation showed discrete sphere polymer morphology, indicating that the inclusion of silver has no significant adverse effect on the polymerisation reaction (GPC and NMR analysis available in ESI†).

TEM investigation revealed silver nanoparticles coating the surface of the polymer spheres. This implies that the PDMS-RAFT surfactant was successful in simultaneously stabilising the growing polymer particle and the silver nanoparticles. The presence of silver in the polymer particles was confirmed by EDX analysis (see ESI†). An additional advantage of this approach is that the versatility of the RAFT agent suggests that this technique will be successful with a wide range of other monomer and metal species.

Closer inspection of the particle surface reveals that the silver nanoparticles are tightly bound to the surface of the polymer particle (Fig. 3). Indeed, the TEM micrographs show that the

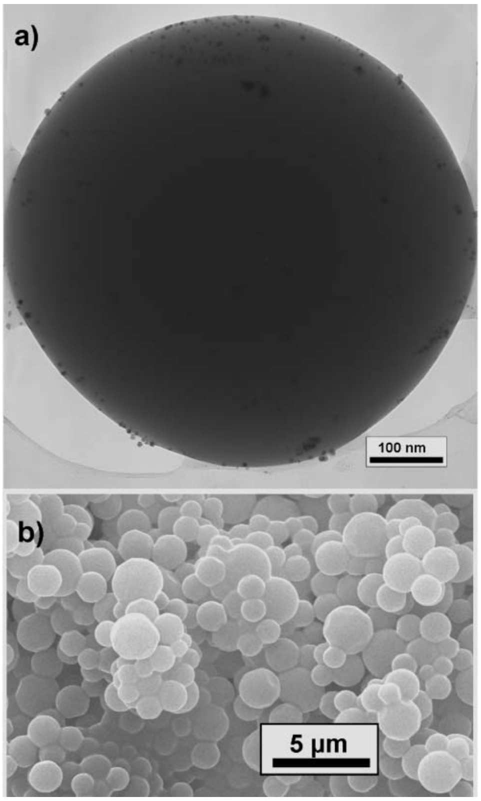

Fig. 2 Silver–polymer nanocomposite. a) Bright field TEM image of silver nanoparticles on polymer. b) Secondary electron SEM image of polymer powder. Note the polymer microspheres are effectively identical to those produced in the absence of silver (Fig. 1b).

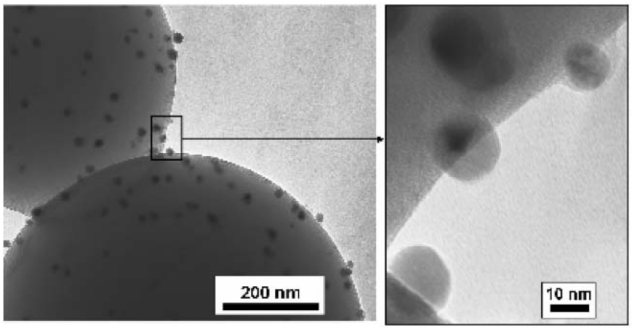

Fig. 3 Bright field TEM image detailing the surface location of the silver nanoparticles. Scale bars represent 200 nm (left), 10 nm (right, enlarged).

nanoparticles generally appear to be partly embedded into the polymer surface. This apparent strong attachment to the polymer particle surface is advantageous as it would imply minimal nanoparticle loss in applications where some friction of particles is required.

All of the nanoparticles observed were within the appropriate size range for favourable applications, mentioned above. All lie within 3–30 nm in diameter with the majority occurring in the 5–20 nm range.

In summary, the use of an appropriately designed RAFT/stabilising agent allows simple and effective synthesis of polymer microspheres decorated with silver nanoparticles in CO_2. The surface location of the nanoparticles gives the polymer powder excellent potential for catalytic, antibacterial and biosensing applications. This synthetic route has the additional advantages of being a single step, one pot reaction that does not require conventional solvents at any stage during the process. Furthermore, the versatility of this technique suggests its applicability for a wide range of polymer nanoparticle composite materials.

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