

Synthesis of Poly(pyrrole)–Silica–Magnetite Nanocomposite Particles

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Pyrrole is polymerised in the presence of ultrafine silica-coated magnetite particles; the resulting colloidal poly(pyrrole)–silica–magnetite nanocomposites have a conducting polymer content of 75 mass% and exhibit superparamagnetism.

Recently the synthesis of conducting polymer nanocomposites has received increasing attention.^{1–5}

We have reported the synthesis of stable colloidal dispersions of both poly(aniline)–silica and poly(pyrrole)–silica nanocomposites using ultrafine silica sols.^{6–8} With the exception of tin(IV) oxide sols,⁹ our attempts to extend this work to include other inorganic oxides have been disappointing. For example, magnetite sols prepared according to Massart's method¹⁰ simply dissolve under the relatively acidic conditions (1.2 mol dm⁻³ HCl) required for aniline polymerisation and are flocculated by the relatively high ionic strength of the FeCl₃ [or (NH₄)₂S₂O₈] oxidant solutions required for pyrrole polymerisation.¹¹ Philipse *et al.*¹² have recently reported the synthesis of stable dispersions of silica-coated magnetite particles. In principle these coated particles should exhibit the colloid stability and surface chemistry of normal silica particles. In the present study we have prepared similar silica-coated magnetite particles and utilised these dispersions to prepare novel colloidal poly(pyrrole)–silica–magnetite nanocomposites (Fig. 1).

Magnetite sols were prepared as aqueous dispersions according to the method of Massart.¹⁰ Thus, aqueous solutions of FeCl₃·6H₂O (160 cm³, 1 mol dm⁻³) and FeCl₂·4H₂O (40 cm³, 2 mol dm⁻³, dissolved in 2 mol dm⁻³ HCl) were mixed prior to their addition to NH₄OH (2000 cm³, 0.7 mol dm⁻³). The resulting precipitate was washed three times by decantation of the aqueous phase followed by addition of H₂O (first two washes) or NEt₄OH (third wash) to give a total volume of 1250 cm³ and pH of *ca.* 12.5. The addition of NEt₄OH resulted in the peptization of the magnetite to form a stable sol. A small fraction of non-peptized aggregates were removed by magnetic sedimentation followed by decantation.

Silica-coated magnetite was prepared by the aqueous deposition of silica from supersaturated silicic acid by a method similar to that described by Philipse *et al.*¹² A solution of 66.4 g sodium silicate (BDH, containing 27.0 ± 1.5 m/v % SiO₂) in 1600 cm³ distilled water was passed through a column containing 120 g 'Duolite C255 (H)' ion exchange resin (BDH) previously regenerated by successive flushing with hot distilled water, 3.0 mol dm⁻³ HCl and cold distilled water. The pH of the eluant was 7.5, and this was raised immediately to pH 9.5 by the addition of a few drops of sodium silicate stock solution in order to prevent homogeneous silica nucleation. This eluant was added to a 3000 cm³ three-necked flask containing 1200 cm³ of the magnetite sol. The pH of this stirred mixture (initially pH 12) was carefully lowered to pH 10 by titration with 0.5 mol dm⁻³ HCl over a period of approximately 1 h. The dispersion was stirred for a further 2 h then purified by dialysis in visking tubing for four days against, on successive days, three 10 l aq. NEt₄OH solutions at pH 10, 9.5 and 8, respectively, and finally distilled water. The

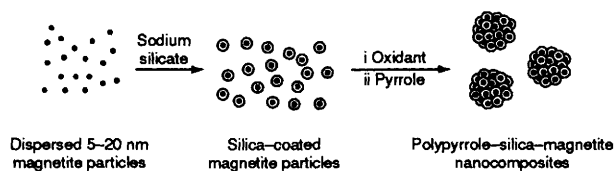


Fig. 1 Schematic representation of the synthesis of poly(pyrrole)–silica–magnetite nanocomposites

resulting silica-coated magnetite sol had a solids content of 0.88 ± 0.02 m/v %.

Pyrrole was polymerised in the presence of the silica-coated magnetite particles according to a procedure first described by Maeda and Armes⁷ for 20 nm silica particles. Pyrrole (0.50 cm³) was added to 150 cm³ of an aqueous dispersion containing 1.0 g (dry mass) silica-coated magnetite particles and 1.92 g (NH₄)₂S₂O₈ (or 4.55 g FeCl₃·6H₂O). This reaction mixture was left stirring at room temp. for at least 16 h. The resulting poly(pyrrole)–silica–magnetite particles were centrifuged (5000 rpm for 30 min) and redispersed in distilled water four times in order to remove ionic impurities and excess silica–magnetite particles. There was a significant excess of silica–magnetite particles left in the decanted supernatant solution after the first centrifugation/redispersal cycle. After the fourth cycle a colourless supernatant was obtained.

Transmission electron microscopy (TEM) studies indicated that the magnetite sol was polydisperse, with particle diameters in the size range 5–30 nm. Once coated with silica, these particles were much more resistant to both solution acidity and electrolyte-induced flocculation. This improved stability is critical for successful nanocomposite syntheses. Our initial attempts to synthesise colloidal poly(pyrrole)–silica–magnetite nanocomposites using the FeCl₃ oxidant to polymerise pyrrole were unsuccessful (only macroscopic precipitates were obtained). However, use of the (NH₄)₂S₂O₈ oxidant resulted in a stable colloidal dispersion. Particle size analysis of this dispersion using a Brookhaven disc centrifuge gave a number-average particle diameter of 180 ± 50 nm, with some evidence for larger sub-micronic aggregates. This value is in reasonable agreement with our TEM studies. Elemental microanalyses of this dried nanocomposite indicated a poly(pyrrole) content of *ca.* 75 mass% [based on its reduced

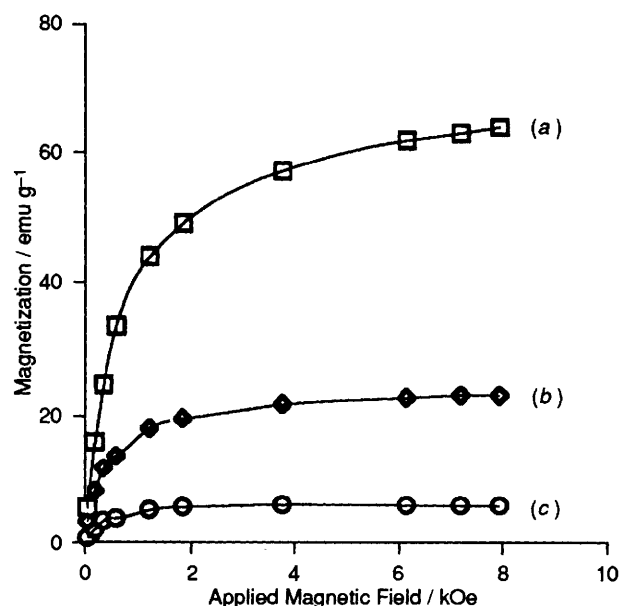


Fig. 2 Magnetisation curves for (a) the dried pristine magnetite sol; (b) the silica-coated magnetite particles; (c) the poly(pyrrole)–silica–magnetite nanocomposite

carbon content relative to bulk poly(pyrrole)]. Its compressed pellet room-temperature conductivity (four-point probe measurements) was approximately $10^{-3} \text{ S cm}^{-1}$. This value is comparable with those obtained on poly(pyrrole)-silica colloids prepared using the same oxidant^{7,8} and has been attributed to partial over-oxidation of the conducting polymer.⁸ FTIR spectroscopy studies (KBr disc) on the poly(pyrrole)-silica-magnetite nanocomposite support this hypothesis since a small carbonyl peak at *ca.* 1700 cm^{-1} is clearly resolved.

Magnetisation measurements were carried out as described previously;¹³ our results are depicted in Fig. 2. Superparamagnetism is exhibited by all three samples. The saturation magnetisation of the magnetite sol was approximately 64 emu g^{-1} ; this plateau value is somewhat lower than the literature value of 92 emu g^{-1} for pure magnetite.[†] The saturation magnetisation values for the silica-coated magnetite particles and the poly(pyrrole)-silica-magnetite nanocomposite were 23 and 6.5 emu g^{-1} , respectively, which correspond to magnetite contents of 36 and 9 mass%. Thus we estimate the silica content of the poly(pyrrole)-silica-magnetite nanocomposite to be approximately 16 mass% by difference.

In summary, our initial 'proof-of-concept' experiments have demonstrated the feasibility of synthesising conducting polymer colloids which exhibit superparamagnetic properties. Our future work will focus on increasing the magnetite content and improving the long-term colloid stability[‡] of these novel dispersions. If these two problems can be overcome we anticipate that such particles may have applications in immunodiagnostic assays.

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Footnotes

[†] Other workers have attributed similar differences in magnetisation between colloidal and bulk materials (*e.g.* for maghemite) to 'surface anisotropy and the presence of a dead magnetic layer'. See ref. 5 and references therein.

[‡] The poly(pyrrole)-silica-magnetite dispersions flocculated irreversibly after storage for one week at room temp. This stability is markedly inferior to our poly(pyrrole)-silica particles which are indefinitely stable under the same conditions (see refs. 7 and 8).

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