

## Novel Colloidal Polyaniline–Silica Composites

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We have prepared novel colloidal polyaniline–silica composites by chemically polymerising aniline in the presence of small silica particles of  $38 \pm 7$  nm diameter; these composites have been characterised by various techniques including thermogravimetry, microanalyses, scanning electron microscopy, photon correlation spectroscopy, visible absorption and FTIR spectroscopy and conductivity measurements.

Polyaniline is generally recognised to be the only air-stable conducting polymer.<sup>1</sup> In its doped, conducting state it is usually an intractable material, but several groups have recently reported the synthesis of block/graft polyaniline copolymers or ring-substituted polyanilines which possess greater processability.<sup>2–6</sup> Our own efforts have primarily focused on the preparation of novel sterically-stabilised dispersions of polyaniline particles.<sup>7–10</sup> In this approach polymeric surfactants containing pendant aniline groups are chemically grafted onto the growing sub-micronic polyaniline nuclei and aggregation is prevented by the so-called 'steric stabilisation' mechanism.<sup>11</sup> Vincent and coworkers have also described similar polyaniline dispersions.<sup>12,13</sup> In the absence of this polymeric surfactant the polyaniline is always obtained as a bulk precipitate.

In the present communication we describe the preparation

and characterisation of a novel colloidal form of polyaniline prepared without the use of conventional polymeric surfactants. Instead, the aniline monomer is polymerised in the presence of small colloidal silica particles ( $38 \pm 7$  nm intensity-average diameter as determined by photon correlation spectroscopy) which act as a high surface area colloidal substrate for the precipitating polyaniline nuclei. Under certain conditions these polyaniline–silica composites are colloidally stable with respect to particle aggregation and therefore represent a more processable form of polyaniline.

The composites were prepared as follows: 0.5–5.0 g of a 50% w/w aqueous solution of colloidal silica was added to 50 ml of a  $1.2 \text{ mol dm}^{-3}$  HCl solution containing 1.57 g ammonium persulfate at room temperature with constant stirring. Aniline (1.0 ml) was then injected and the solution turned green within five minutes. This reaction mixture was

**Table 1** Experimental reaction conditions for the preparation of polyaniline-silica composites

Initial silica concentration (w/v %)	Fraction of polyaniline in composite <sup>a</sup> (wt. %)	Conductivity <sup>b</sup> /S cm <sup>-1</sup>	Physical appearance
0.5	62.5	—	Precipitate
1.0	43.4	—	Precipitate
2.0	30.5	—	Trace colloid
2.3	21.3	2.8	Partially colloidal
2.7	21.7	0.4	Partially colloidal
2.9	21.7	7 × 10 <sup>-2</sup>	Stable colloid
4.8	18.7	0.2	Stable colloid

<sup>a</sup> As determined by thermogravimetry. <sup>b</sup> Solid-state d.c. conductivity measurements on compressed pellets.

stirred for a further 16 h prior to centrifugation at 5000 rev. min<sup>-1</sup> for 30 min. The resulting dark green sediment was redispersed in 1.2 mol dm<sup>-3</sup> HCl using an ultrasonic bath. This centrifugation-redispersion cycle was repeated twice more in order to remove excess of nonadsorbed silica particles from the composites.

The results of these preparations are summarised in Table 1. It is clear that the minimum silica concentration required to produce stable colloidal dispersions of polyaniline is *ca.* 3.0% w/v. Below this concentration a macroscopic polyaniline-silica precipitate was obtained. Both the stable colloids and the precipitates were characterised by C,H,N microanalysis and thermogravimetry in order to assess their polyaniline content. In the latter method the composite was heated to 600 °C and the polyaniline content was then determined from the observed mass loss after allowing for the water content of the silica particles (typically 10%). These two independent methods were generally in good agreement.

Above a silica particle concentration of *ca.* 2.0–2.4% w/v, the weight fraction of polyaniline in the composite (and hence their electrical conductivity, as measured by conventional four-point probe techniques) was effectively constant. This observation is in marked contrast to our results for macroscopic composites of polyaniline-silica prepared using large (1000 nm diam.) silica particles.<sup>14,15</sup> In this latter system the polyaniline loading is easily controlled by varying the initial silica particle concentration and these composites exhibit typical conductivity percolation threshold behaviour as expected.

Simple calculations based on the thermogravimetry data suggest that the high mass loading of silica in the composites is best explained by assuming that the particles are simply loose clusters or aggregates of silica particles held together by polyaniline which acts as a bridging flocculant or 'binder'.

In control experiments we used photon correlation spectroscopy to monitor the particle size of the silica particles under the actual colloid synthesis conditions prior to the addition of aniline monomer [1.57 g of (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> in 50 ml of 1.2 mol dm<sup>-3</sup> HCl]. No change in particle size was observed over a 2 h period; thus there is no detectable *pre-aggregation* of the silica particles prior to the *in situ* polymerisation of aniline.

The formation of polyaniline was confirmed by visible absorption spectroscopy on the diluted, redispersed colloids and FTIR spectroscopy on the dried composite powders dispersed in KBr discs. The spectra were consistent with those previously reported in the literature.<sup>1</sup>

We examined the morphology of these polyaniline-silica composites by scanning electron microscopy. The particles appear to be approximately spherical and are 200–500 nm in diameter. There is some evidence that these composite particles do indeed consist of aggregates of the original small

silica particles, although the instrument's resolution is insufficient to confirm this hypothesis unequivocally. Preliminary photon correlation spectroscopy experiments on these diluted colloidal dispersions give particle sizes which are in good agreement with our electron microscopy studies. The observed particle size is similar to that for the polymer-stabilised polyaniline colloids reported by Vincent and Waterson<sup>13</sup> and is consistent with the observed rapid sedimentation of our dispersions at relatively low centrifugation rates. A complete study of the particle morphology and size distributions of these novel polyaniline-silica colloids using various sizing techniques will be published elsewhere.<sup>16</sup>

Other oxidants for the polymerisation of aniline such as KIO<sub>3</sub> also lead to the formation of stable colloidal dispersions. Evaporation of the dispersion medium does not result in coherent films but instead produces powdery deposits. We are currently examining the use of film-forming latexes as additives to colloidal dispersions of these polyaniline-silica composites so as to promote uniform film formation.<sup>15</sup>

Our initial attempts to prepare analogous polypyrrole-silica colloidal composites using FeCl<sub>3</sub> in H<sub>2</sub>O were unsuccessful. However, the use of 1.2 mol dm<sup>-3</sup> HCl instead of H<sub>2</sub>O resulted in the formation of stable polypyrrole-silica dispersions. This observation suggests that composite particle formation is promoted by some unknown pH-dependent process. The actual stabilisation mechanism is unknown but in view of the high ionic strength of the dispersion medium (1.2 mol dm<sup>-3</sup> HCl) it is highly unlikely that these conducting polymer-silica colloids are charge-stabilised.

In conclusion we have discovered a novel and convenient method for the preparation of colloidal polyaniline which utilises commercially available small silica particles as dispersants rather than tailor-made polymeric stabilisers.

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