Surface Composition of Surfactant-stabilised Polypyrrole Colloids

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We have examined a colloidal dispersion of surfactant-stabilised polypyrrole particles by surface-enhanced Raman spectroscopy (SERS), time-of-flight secondary ion mass spectroscopy (TOF-SIMS) and X-ray photoelectron spectroscopy (XPS). These surface-specific techniques have enabled us to probe the surface composition of the conducting polymer particles. All three techniques indicate that the polypyrrole component is present at (or near) the particle surface: this observation is consistent with the relatively high pressed-pellet conductivities exhibited by these colloids. Our TOF-SIMS results suggest that the surfactant stabiliser is the dominant component in the first monolayer. Similarly, our wide-scan XPS spectra indicate that the sulfur/nitrogen surface atomic ratio of the polypyrrole colloid is significantly higher than that of polypyrrole bulk powder; curve fitting of the corresponding core-line sulfur spectra confirm that a significant proportion of this excess sulfur is due to the sulfonate-based surfactant. Thus, both our TOF-SIMS and XPS studies confirm that the surface of the polypyrrole particles is distinctly 'surfactant-rich', which is consistent with the observed long-term colloidal stability of these dispersions.

There has been increasing interest in the preparation and characterisation of conducting polymer colloids *via* dispersion polymerisation.[1–12] In this approach the conducting polymer is usually synthesised in the presence of a polymeric stabiliser which is adsorbed onto the precipitating microscopic conducting polymer nuclei and prevents their aggregation *via* a steric stabilisation mechanism.[13] These conducting polymer systems are more processable than the intractable bulk powders usually obtained from conventional chemical syntheses. In addition, such dispersions may have potential applications as novel 'marker' particles for use in visual agglutination immunodiagnostic assays.[14]

We have recently attempted to examine the nature of the outer layer of polymeric stabiliser surrounding the conducting polymer particles. For example, our combined photon correlation spectroscopy experiments,[15] disc centrifuge studies[16] and long-term colloid stability observations[17] on the poly(4-vinylpyridine-co-*n*-butyl methacrylate)-stabilised polypyrrole colloid system have provided direct experimental evidence for a relatively thick and uniform outer layer of solvated polymeric stabiliser. Our transmission and scanning electron microscopy studies confirm that these dispersions retain their spherical morphology in the solid state.[18] Thus, in view of the electrically insulating nature of the polymeric stabiliser, it is remarkable that these conducting polymer composite particles exhibit such high solid-state conductivities (typically 0.1–1.0 S cm⁻¹). A possible explanation for this observation is that the outer layer of polymeric stabiliser is either very thin (to allow efficient electron tunnelling between polypyrrole core particles) and/or non-uniform in the solid state. In order to distinguish between these two possibilities we examined the solid state nanomorphology of related poly(vinyl alcohol)-stabilised polypyrrole colloids by scanning tunnelling microscopy (STM).[19] Our observations were consistent with a patchy, non-uniform stabiliser layer on the polypyrrole particles in the solid state. We note that Deslandes *et al.* have recently suggested a similar model for poly(*N*-vinylpyrrolidone)-stabilised polystyrene particles on the basis of their XPS and TOF-SIMS experiments.[20]

In the present paper we have characterised a new surfactant-stabilised polypyrrole colloid[21] using three well established surface science techniques: TOF-SIMS, SERS and XPS. The aim of this work was to examine the nature of

the surface of the surfactant-stabilised conducting polymer particles in the solid state at the molecular level.

Experimental

Preparation of Surfactant-stabilised Polypyrrole Colloid

The polypyrrole colloid synthesis was carried out as follows: 10.0 g sodium dodecylbenzenesulfonate (SDBS) and 7.85 g $(NH_4)_2S_2O_8$ oxidant were co-dissolved in 200 ml de-ionized water at 20 °C in a 250 ml glass bottle to give a turbid solution. Then pyrrole monomer (2.0 ml) was injected quickly *via* a syringe and the reaction vessel sealed before being transferred to a roller mill (Unimix model 840) for 4 h. The resulting black, viscous colloidal dispersion was centrifuged at 20 000 rpm for 75 min to produce a black sediment, which was then redispersed in de-ionised water simply by mechanical stirring. Finally, this redispersed colloid was filtered through a glass sinter under gravity in order to remove traces of non-redispersed material. Elemental microanalysis data for the purified, dried colloid were as follows: C 53.12%; H 6.90%; N 6.15%; S 8.45% (average of duplicate analyses for CHN). Conventional four-point probe conductivity measurements on compressed pellets at room temperature indicated a conductivity of *ca.* 10^{-2} S cm⁻¹.

Electrochemical Synthesis of Dodecylbenzenesulfonate-doped Polypyrrole Film

The synthesis was based on a procedure described by Wernet *et al.*[22] An EG&G Princeton Applied Research potentiostat/galvanostat model 273 was used in conjunction with a 1 × 1 cm² silica sol-coated aluminium disc working electrode and a Ag/Ag^+ reference electrode (see below for silica sol coating details). The polymerisation solution contained 3.48 g SDBS and 2.0 ml pyrrole in 100 ml distilled water. A potential of 750 mV was applied until 0.30 C of charge had been passed; this resulted in the deposition of a thin, black polypyrrole film on the gold electrode. In subsequent SERS experiments a thin overlayer of gold was sputter-coated onto the top of the resulting polypyrrole-coated (middle layer) and silica-coated (underlayer) aluminium disc electrode.

SEM

The particle morphology of the surfactant-stabilised poly-pyrrole colloid was examined using a Leica Stereoscan 420 instrument operating at 30 kV. The sample was mounted on a double-sided adhesive carbon disc and sputter-coated with a thin layer of gold to prevent sample-charging problems.

TOF-SIMS

Samples were mounted on an indium metal substrate prior to examination. A Kratos Prism TOF-SIMS instrument was used to acquire data. The primary beam consisted of 25 KeV $^{69}Ga^{+}$ ions produced in 100 ns duration pulses. The beam current was *ca.* 600 pA and 1×10^{6} pulses were used to produce each spectrum. Areas between 1 mm $\times$ 1 mm and 333 μm $\times$ 333 μm were examined. These conditions correspond to the 'static' mode where the monolayer lifetime is greater than the analysis time.[23]

SERS

SERS spectra were recorded using a Bruker FRA 106 spectrometer equipped with a 1064 nm laser (max. power 300 mW). Aluminium specimen stubs were first roughened using 400 mesh carborundum paper prior to spin-coating with one drop of a 10 wt.% colloidal silica sol in a 70/30 water/methanol solvent mixture. This layer of silica particles was then coated with a *ca.* 50 nm gold overlayer using a Bio-Rad Turbocoater. It was generally found that only 20% of the laser power was required owing to the exceptionally strong SERS signal from the polypyrrole. Each SERS spectrum was an average of at least 500 scans and was recorded at a spectral resolution of 4 cm^{-1}.

XPS

Experiments were carried out on compressed pellets of both bulk powder and colloidal polypyrrole samples. Data were collected using a Kratos AXIS imaging X-ray photoelectron spectrometer using an unmonochromated 1254 eV Mg-Kα X-ray source at an operating vacuum of at least 10^{-8} Torr. Pass energies were set at 80 eV for survey spectra and 40 eV for core line spectra. Sample acquisition times were typically 3 and 10 min for the survey spectra and core line XPS spectra, respectively. Peak positions were calibrated against C 1s (285.0 eV). The spectra were analysed using a SPARC work station equipped with VISION software version 1.2.2. Curve-fitting was carried out using mixed-shape peaks (60% Gaussian, 40% Lorentzian).

Results and Discussion

Our SEM studies on the SDBS-stabilised polypyrrole particles revealed an approximately spherical, polydisperse morphology with particle diameters in the range 300 to 500 nm (see Fig. 1). This particle morphology is markedly different to the non-spherical particles reported in our initial communication:[21] we now believe that this earlier observation by TEM was probably an artifact. The reduced nitrogen content of the colloid (6.15%) relative to that of 'bulk powder' polypyrrole made in the absence of surfactant (14.55%) indicates a relatively high surfactant content of 58%; we have recently observed similarly high stabiliser contents with other conducting polymer colloid systems.[9] This high surfactant loading suggests that the DBSA surfactant anion acts as the major dopant anion species for the cationic polypyrrole chains (rather than the sulfate dianion derived from the per-
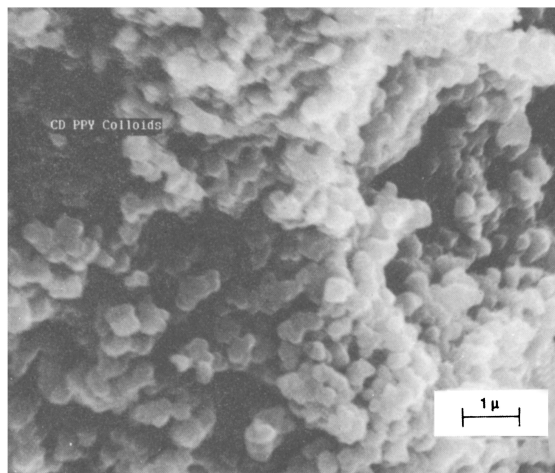

Fig. 1 SEM micrograph of the SDBS-stabilised polypyrrole particles. The particles are approximately spherical and are somewhat polydisperse, with a particle size range of 300–500 nm. This specimen was sputter-coated with gold to minimise sample-charging problems.

sulfate oxidant), as well as a surfactant stabiliser for the polypyrrole particles.

Over the last two decades many groups have shown that SERS is a surface-sensitive technique for the characterisation of both small molecules[24,25] and polymers[26–28] adsorbed onto various 'atomically rough' metal substrates. Under favourable conditions Raman intensity enhancement factors of up to 10^{6} have been observed. Thus this technique has been used successfully to study molecular adsorption processes at the sub-monolayer level. Unlike conventional Raman or resonance Raman spectroscopy, SERS is highly surface-specific. Usually little or no intensity enhancement is observed for molecular species which are further than 50–100 Å from the metal substrate.[29] There have been very few reports of the use of SERS in the characterisation of conducting polymers.[30–33] Most have examined electrochemically synthesised thin films of conducting polymers grown on metal electrodes.[31–33] As far as we are aware, there have been no previous reports of the SERS technique being used to examine the surface composition of conducting polymer colloid particles.

An SERS spectrum of the surfactant-stabilised colloidal polypyrrole particles spin-coated onto a roughened gold surface (see Experimental) at a sub-monolayer particle concentration is depicted in Fig. 2. In our control experiments no SERS spectra could be obtained from the same colloid sample spin-coated onto silica-coated aluminium substrates in the absence of gold. Furthermore, a polypyrrole film electrodeposited onto a similar silica-coated aluminium substrate also gave no SERS spectrum but when this latter polypyrrole sample was sputter-coated with a thin overlayer of gold a strong SERS spectrum was immediately detected under the same experimental conditions (see Fig. 2). Thus we are confident that the spectra depicted in Fig. 2 are due to a genuine SERS effect rather than normal Raman scattering. All the observed spectral features are attributable to doped polypyrrole,[34] with no evidence for the presence of the SDBS surfactant stabiliser (in our subsequent control experiments with roughened gold surfaces no SERS spectra could be obtained for adsorbed monolayers of the pure SDBS surfactant, in either its free acid or its sodium salt form). This result indicates that the polypyrrole 'core' of the surfactant-stabilised polypyrrole particles is in close proximity with the roughened gold surface. Thus, the adsorbed outer layer of the surfactant
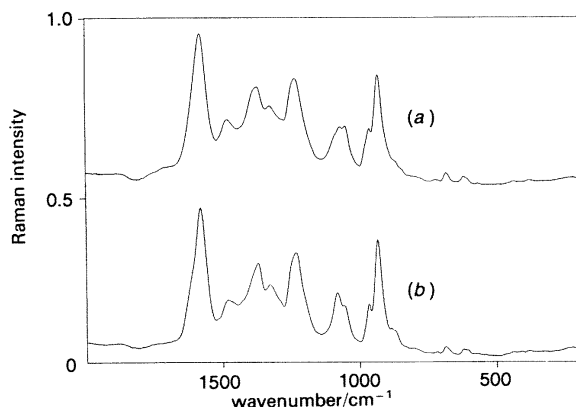
Fig. 2 SERS for (a) SDBS-stabilised colloidal polypyrrole particles spin-coated onto a roughened gold substrate and (b) electrodeposited polypyrrole film synthesised using SDBS as the electrolyte salt

stabiliser surrounding the polypyrrole particles must be either 'patchy' or relatively thin (<150 Å). We note that this SERS observation is consistent with the relatively high macroscopic solid state conductivities observed for these colloidal polypyrrole particles (see Experimental).

SIMS (and related techniques such as the atom probe, a combined field ion microscope and mass spectrometer) have been used to characterise conducting polymer samples in a variety of physical forms, e.g. thin films,[35,36] coatings on textile fibres[37] and bulk powders.[38] In particular, it has been shown that negative ion SIMS can provide useful structural information regarding the nature of the dopant anion species.[37,38] The SIMS technique is much more surface-specific than SERS and probes only the first monolayer of the surface of the sample. TOF-SIMS is simply a more refined version of SIMS and provides greater sensitivity towards higher mass fragments. An Italian group have recently studied the doping/undoping processes in electrochemically synthesised polybithiophene films using this latter technique.[39]

Our negative ion TOF-SIMS spectra are shown in Fig. 3. The pure SDBS surfactant spectrum shown in Fig. 3(a) is in excellent agreement with the literature.[40] This spectrum is almost identical to that of the SDBS-stabilised colloidal particles in the 0–40 u range, except that an additional peak at 26 u is seen in the colloid spectrum [see Fig. 3(b)]. This peak is also prominent in the TOF-SIMS spectrum of our polypyrrole bulk powder sample [see Fig. 3(c)] and has been attributed to $C-N^-$ fragments by Abel et al. in their recent studies on electrochemically grown polypyrrole films.[41] Similarly, the negative ion TOF-SIMS spectra of the pure surfactant and colloidal polypyrrole samples are almost indistinguishable in the 50–400 u range (see Fig. 4), except for an additional peak at 97 u in the latter spectrum, which is presumably due to the SO_4^{2-} and/or HSO_4^- dopant anion species (the peaks at 311 and 339 u are the C_{10} and C_{14} alkyl isomers of the, supposedly, pure C_{12} alkyl chain of the surfactant which has its $C_{12}H_{25}C_6H_4SO_3^-$ parent ion at 325 u). Thus, our TOF-SIMS data indicate that the polypyrrole particles are coated with an adsorbed monolayer of SDBS surfactant. On the other hand, the additional peaks due to the polypyrrole component at 26 and 97 u suggest that this surfactant overlayer is patchy.

Many groups have reported the successful use of XPS for the characterisation of conducting polymers.[42–50] These studies have focused almost exclusively on chemically synthe-
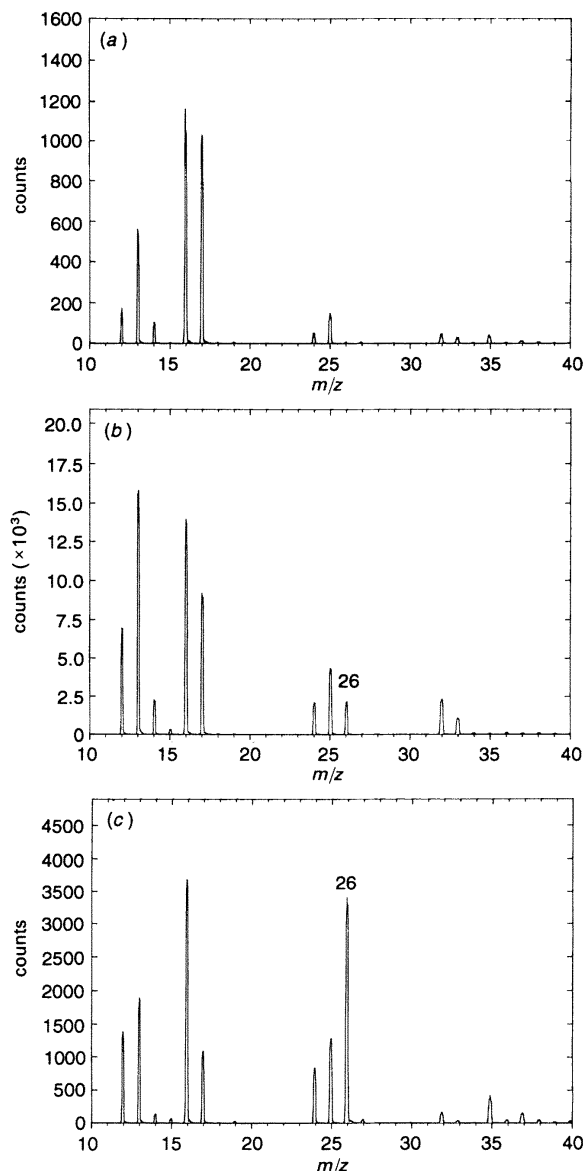

Fig. 3 Negative ion TOF-SIMS spectra in 0–40 u low mass range for (a) the SDBS surfactant; (b) the SDBS-stabilised colloidal polypyrrole particles (note the additional peak at 26 u due to $C-N^-$ fragments from the underlying polypyrrole particle core); (c) the polypyrrole bulk powder (note that the 26 u peak due to the $C-N^-$ fragment is more prominent in this latter spectrum)

sised bulk powders or electrochemically-synthesised thin films. Since XPS has a typical sampling depth of 20–50 Å this technique has proved particularly useful in assessing the surface oxidation and degradation chemistry of conducting polymers.[49,50]

In our experimental strategy we utilised the sulfur atoms in the surfactant component and the nitrogen atoms in the polypyrrole component as elemental 'markers'. Thus, measuring the sulfur/nitrogen atom ratios by XPS allowed us to make a semi-quantitative assessment of the surfactant/conducting polymer surface composition of the colloidal particles. We have recently used a similar 'elemental marker' approach to characterise the surface composition of conducting polymer–
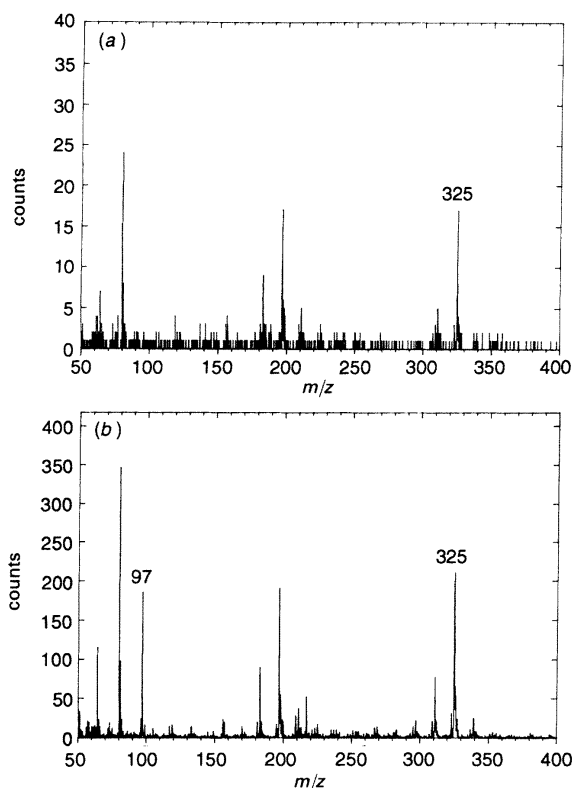
Fig. 4   Negative ion TOF-SIMS in 50–400 u high mass range for (a) the SDBS surfactant; (b) the SDBS-stabilised colloidal polypyrrole particles (note the additional peak at 97 u due to HSO_4^-/SO_4^{2-} dopant anions from the underlying polypyrrole particle core)
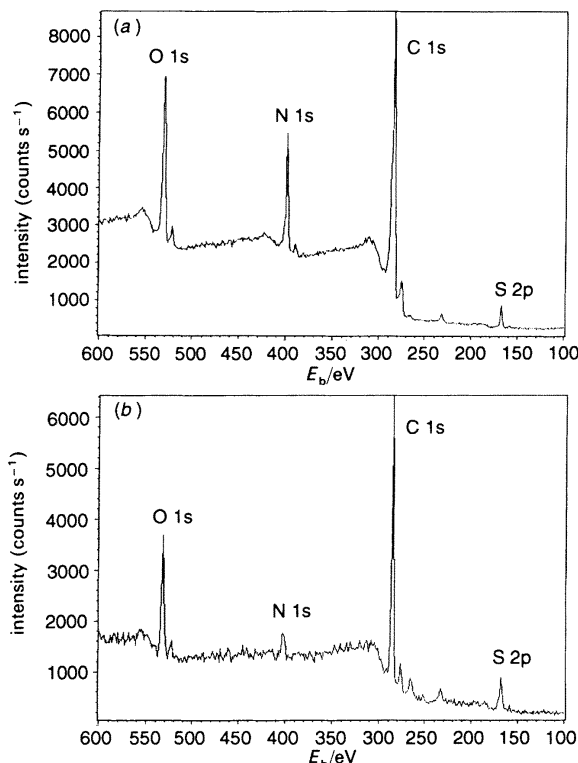

Fig. 5   XP survey spectra for (a) bulk polypyrrole powder and (b) SDBS-stabilised colloidal polypyrrole particles. Note the larger sulfur peak (relative to nitrogen) in the latter spectrum.

silica nanocomposite particles. In this latter system the two elements, silicon and nitrogen, are unique to each component and this simplifies the interpretation of the data. In contrast, sulfur is not a unique elemental marker in the present surfactant-stabilised colloid system since it is present in both the SDBS surfactant molecules (in the sulfonate group) and also in the polypyrrole (as sulfate dopant anions).

Our XPS survey spectra of both the sulfate-doped polypyrrole bulk powder and the SDBS-stabilised colloidal polypyrrole particles are depicted in Fig. 5. The polypyrrole bulk powder sample contains both nitrogen (due to the cationic polypyrrole chains) and sulfur (due to the sulfate dopant anions). The sulfur/nitrogen surface atomic ratio in this sample is *ca.* 0.16. Since the sulfate species is a di-anion, this suggests a doping level of 0.32 for the polypyrrole, which is in reasonable agreement both with polypyrrole dopant levels reported in the literature and also our earlier work.[21]

Turning our attention to the survey spectrum of the SDBS-stabilised polypyrrole colloid we calculate a sulfur/nitrogen surface atomic ratio of 0.97. We believe that this surface excess of sulfur (relative to the bulk powder spectrum) is best explained by the presence of the SDBS stabiliser adsorbed at the surface of the polypyrrole particles, in addition to the sulfonate/sulfate dopant anions. Accordingly, we examined the S 2p core-line spectra of both the 'bulk powder' and colloidal polypyrrole samples for evidence of the SDBS surfactant. Curve fitting of the former spectrum confirmed the presence of only one type of sulfur atom (see Fig. 6). In contrast, two sulfur species can be identified in the sulfur spectrum of the polypyrrole colloid. With the aid of $(NH_4)_2SO_4$

and SDBS control samples the sulfur species at 169.3 eV (referenced to C 1s, 285.0 eV) was assigned to the sulfate dopant anion, whilst the sulfur species at 168.5 eV was assigned to the sulfonate anion of the SDBS surfactant. From their relative peak areas we estimate that the surface concentrations of the SDBS surfactant and sulfate anion are approximately equal.
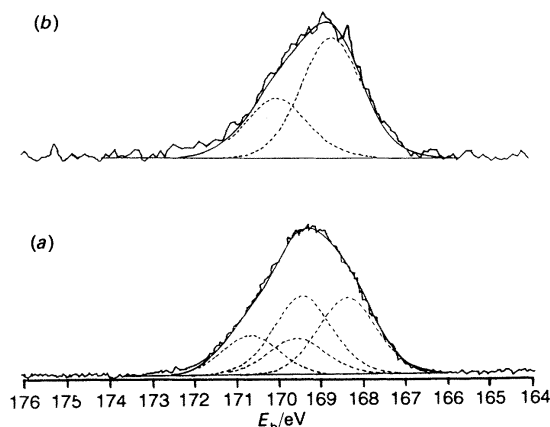

Fig. 6   (a) S 2p core-line XPS of the SDBS-stabilised colloidal polypyrrole particles. Curve-fitting confirms that this spectrum contains two types of sulfur atoms: sulfonate species due to the adsorbed SDBS surfactant and sulfate species due to the dopant anions. (b) S 2p core-line XPS of the sulfate-doped polypyrrole bulk powder synthesised in the absence of surfactant. Note that only one type of sulfur atom is present in this latter spectrum.

Thus our XPS studies confirm the presence of both the SDBS surfactant and the polypyrrole within the uppermost 20–50 Å of the particles in the solid state. These observations are in agreement with our TOF-SIMS results and are consistent with the currently accepted theories of charge and steric stabilisation in colloid science.[13,52–55] Thus a solvated, adsorbed outer layer of SDBS surfactant molecules provides an electrosteric barrier which is a prerequisite for the observed long-term colloid stability of the polypyrrole particles. We note that Davies *et al.* and other workers[56–60] have recently utilised XPS and SIMS techniques to examine both charge- and polymer-stabilised polystyrene latex particles. These elegant studies also confirm the presence of the stabilising species at the particle surface and are therefore in good agreement with our observations.

The actual structure of the adsorbed SDBS surfactant layer is as yet unclear. Given the hydrophobic nature of the C_{12} alkyl chain we would expect this part of the surfactant to be adsorbed onto the surface of the polypyrrole particles in their aqueous, dispersed form. However, in view of the relatively high surfactant content of the colloidal particles, a more complex lipid bilayer structure such as that found in biological systems cannot be ruled out at present.

The solid-state electrical conductivity of 'bulk powder' polypyrrole synthesised in the absence of surfactant using the $(NH_4)_2S_2O_8$ oxidant is 10^{-1} S cm^{-1}.[61] This value is somewhat lower than that obtained when using milder oxidants such as $FeCl_3$ (typically 1–10 S cm^{-1}). We have recently suggested that this difference is probably due to over-oxidation of the conducting polymer: the presence of carbonyl groups in the FTIR spectrum of $(NH_4)_2S_2O_8$-synthesised polypyrrole is consistent with this hypothesis.[62] We have generally found that the conductivities of conducting polymer colloid systems are approximately an order of magnitude lower than the conductivity of bulk powder polypyrrole made under the same conditions.[2–9] Thus the observed conductivity of 10^{-2} S cm^{-1} for the SDBS-stabilised colloid is consistent with our previous work. This relatively high value suggests that the surfactant stabiliser is probably rather inhomogeneously distributed on the particle surface in the solid state. We believe that the SDBS surfactant tends to accumulate as 'islands', leaving 'bare patches' of the polypyrrole 'core' particles. The resulting microscopic interparticle contacts for the conducting polymer component accounts for the observed macroscopic solid state electrical conductivity. This hypothesis is consistent with our XPS and TOF-SIMS data and is similar to the ideas proposed by Deslandes *et al.* for the surface of μm-sized polymer-stabilised polystyrene latexes.[20]

Conclusions

Our TOF-SIMS results indicate that the polypyrrole particles are coated with an adsorbed monolayer of SDBS surfactant molecules. There is also some evidence for the presence of the underlying polypyrrole 'core' particles. On the other hand, our SERS studies clearly confirm the presence of the conducting polymer component at, or close to, the surface of the surfactant-stabilised particles but do not detect the SDBS surfactant. We believe that these apparently contradictory observations can be rationalised in view of (i) the very low SERS activity observed for the SDBS surfactant in our control experiments and/or (ii) the rather differing sampling depths for these two surface techniques (only the first monolayer for TOF-SIMS but up to 50–100 Å for SERS).

Our XPS studies confirm that the first few nanometres of the surface of the SDBS-stabilised polypyrrole particles are surfactant-rich. Thus our XPS and TOF-SIMS data are in good agreement and are consistent with the observed long-term colloid stability of the polypyrrole particles in aqueous media. On the other hand, the close proximity of the conducting polymer component at, or near, the surface of the polypyrrole particles (confirmed by all three techniques) suggests the possibility of a solid-state conduction mechanism based on direct interparticle contacts. Thus our surface composition observations are also consistent with the relatively high electrical conductivities observed for these materials in the solid state. In conclusion, the combined use of SERS, TOF-SIMS and XPS, has provided us with a useful insight into the surface composition of SDBS-stabilised polypyrrole colloids.

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