One-Pot Preparation of Conducting Polymer-Coated Silica Particles: Model Highly Absorbing Aerosols

Joseph R. Lovett, Lee A. Fielding, Steven P. Armes, and Ronald Buxton*

Near-monodisperse 0.50 μm and 1.0 μm silica particles are surface-modified using 3-(trimethoxysilyl)propyl methacrylate (MPS) and subsequently coated by aqueous deposition of an ultrathin polypyrrole (PPy) overlayer to produce PPy-coated silica particles. The targeted degree of MPS modification and PPy mass loading are systematically varied to optimize the colloidal stability and PPy coating uniformity. MPS surface modification is characterized by contact angle goniometry and the PPy overlayer uniformity is assessed by scanning electron microscopy. HF etching of the silica cores produces hollow PPy shells, thus confirming the contiguous nature of the PPy overlayer and the core–shell morphology of the original particles. Four-point probe measurements and XPS studies indicate that the electrical conductivity of pressed pellets of PPy-coated silica particles increases with PPy surface coverage. Colloidal stabilities of the bare, MPS-modified, and PPy-coated silica particles in aqueous solution are assessed using disk centrifuge photosedimentometry. MPS surface modification results in weak flocculation, with subsequent PPy deposition causing further aggregation. In contrast, white light aerosol spectrometry indicates a relatively high degree of dispersion for PPy-coated silica particles in the gas phase. Such PPy-coated silica particles are expected to be useful mimics for silica-rich micrometeorites and may also serve as a model highly absorbing aerosol.

1. Introduction

Polypyrrole has been recognized to be an electroactive material for at least three decades.[1] This relatively air-stable organic conducting polymer is readily synthesized in water at room temperature in the form of an insoluble bulk powder using chemical oxidants such as $FeCl_3$ or $(NH_4)S_2O_8$.[2] Its intrinsically poor processability can be alleviated by preparing colloidal dispersions of polypyrrole particles using various stabilizers, such as water-soluble polymers,[3] surfactants[4] or ultrafine silica sols.[5] Alternatively, polypyrrole can be deposited as an ultrathin overlayer onto sterically-stabilized latexes from aqueous solution to produce well defined core–shell particles.[6] A wide range of potential applications have been suggested for such core–shell latexes, including immunodiagnostic assays,[7] electrorheological suspensions,[6f] reversible adhesives,[8] or as recoverable high surface area supports for heterogeneous catalysis using precious metals.[9] For the past decade or so,[10] we have evaluated polypyrrole-coated latexes in collaboration with space science research groups based in the UK,[10a,11] Germany,[12] and the USA.[12] In this application, the electrically conductive polypyrrole overlayer allows the efficient accumulation of surface charge, which in turn enables the particles to be accelerated up to hypervelocities (>1 km s^{-1}) using a 1.5 MV applied field. This is comparable to the speeds attained by micro-meteorites (or “cosmic dust”) found in outer space. Given their narrow particle size distributions, low densities and high carbon contents, polypyrrole-coated polystyrene latex particles are ideal synthetic mimics for understanding the behavior of carbonaceous micro-meteorites. Laboratory experiments using these model projectiles have provided useful insights for interpreting data obtained from both the CASSINI and STARDUST space missions.[10a,11,12] In these studies, the ultrafast electronics used in the experimental set-up allows velocity selection of individual polypyrrole-coated latexes, so that aggregates or clumps can be excluded from the analysis, if desired. In this context, the strong propensity for rigorously dried polypyrrole-coated latex particles to form a long-lived “smoke” or aerosol on gentle agitation is rather striking compared to the behavior of pristine polystyrene latex particles, which remain clumped together. This phenomenon is not properly understood, but presumably the high cationic surface charge conferred by the polypyrrole coating leads to strong electrostatic repulsion between neighboring latex particles in the solid state, which in turn facilitates their efficient dispersal in air.[10a] It is well known that micrometer-sized particles can be lung irritants[13] and there is also increasing pressure to introduce legislation to regulate the generation and handling of (and exposure to) nanoparticles in the industrial workplace.[14] Thus near-monodisperse model aerosol particles are expected to be extremely useful for the calibration of particle size analyzers, sieves, respiratory masks, and other devices.[14b,15]

An early attempt by Armes et al.[16] to coat micrometer-sized silica particles with an ultrathin polypyrrole overlayer only led to a highly globular and rather inhomogeneous coating. This is

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J. R. Lovett, Dr. L. A. Fielding, Prof. S. P. Armes
Department of Chemistry
University of Sheffield
Brook Hill, Sheffield, South Yorkshire, S3 7HF, UK
E-mail: s.p.armes@sheffield.ac.uk
Dr. R. Buxton
Particle Technology Ltd., Station Yard Industrial Estate
Hatton, Derbyshire, DE65 5DU, UK

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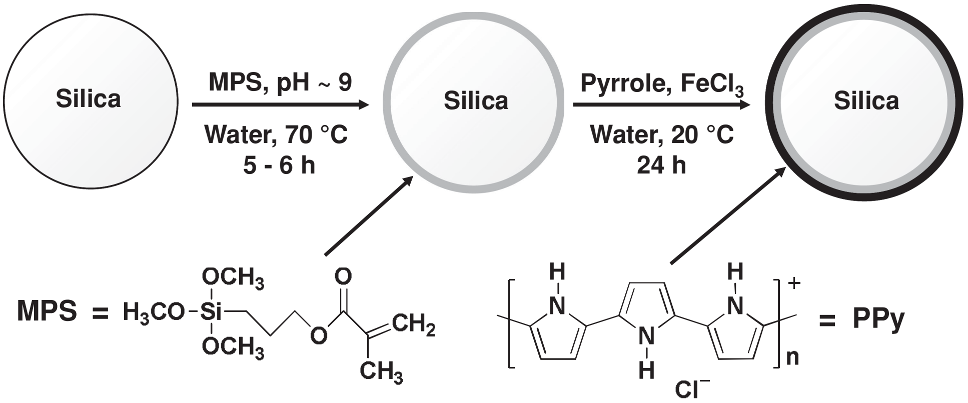

Figure 1. Schematic representation of the surface modification of silica using 3-(trimethoxysilyl)propyl methacrylate (MPS), and subsequent coating of these hydrophobically-modified particles with an ultrathin layer of polypyrrole (PPy) via aqueous deposition.

mainly due to the high density of anionic silanol groups on the silica surface: it is well known that polypyrrole is preferentially deposited onto hydrophobic substrates, rather than hydrophilic substrates.[17] More recently, there have been several literature reports claiming that more uniform polypyrrole deposition can be achieved, provided that the silica particles are pre-treated with either silanes or a monolayer of poly(*N*-vinylpyrrolidone).[18] However, as far as we are aware, the degree of dispersion of the resulting polypyrrole-coated silica particles in either aqueous solution or in the gas phase has never been properly assessed.

In the present work, we have undertaken a systematic study to modify the surface of micrometer-sized silica particles with a cheap commercial silane so as to optimize the subsequent deposition of polypyrrole. The resulting core–shell particles have been extensively characterized in terms of their chemical composition, surface morphology, degree of dispersion in aqueous solution and pressed pellet electrical conductivities. Previously, highly absorbing model aerosols have been generated via atomization of aqueous solutions of dyes such as nigrosin, followed by analysis using a differential mobility analyzer (DMA).[19,20] In contrast, in the present work we demonstrate that model highly absorbing monodisperse aerosols can be spontaneously generated from dry powders of polypyrrole-coated silica particles and subsequently sized using a light scattering technique that is widely used for characterizing airborne particulates.

2. Results and Discussion

It is well-known that the controlled deposition of PPy from aqueous solution onto relatively hydrophobic polystyrene latex particles leads to a relatively smooth, contiguous and uniform overlayer.[6d,e] However, PPy deposition from aqueous solution onto less hydrophobic latexes such as poly(methyl methacrylate) latex[6g,11,16,21] leads to a much less uniform, more patchy, conducting polymer overlayer, as judged by SEM studies.

Several research groups have reported the deposition of PPy onto modified silica particles.[18] Surface modification has been achieved either by physical adsorption of poly(*N*-vinylpyrrolidone)[18a] or by chemical grafting of various silane coupling agents.[18b-d] Of particular relevance to the present work, Yang et al.[18c] employed 3-(trimethoxysilyl)propyl methacrylate (MPS) to hydrophobically modify silica particles but optimum deposition conditions were not identified and it was found that the resulting PPy overlayer was rather inhomogeneous. As far as we are aware, there have been no studies focusing on the systematic variation of the degree of surface modification of silica particles in order to achieve optimum deposition of PPy overlayers. This is rather surprising, since this important parameter should influence the PPy overlayer uniformity and, in turn, affect the colloidal stability of the PPy-coated silica particles in aqueous solution. Moreover, PPy-coated particles have never been evaluated as model aerosols. In the present study, we focus on the surface modification of near-monodisperse silica particles of 0.50 or 1.0 μm diameter using MPS, followed by PPy deposition from aqueous solution using $FeCl_3$ oxidant (see **Figure 1**).

For the initial silanization, a fixed mass of silica particles was utilized and the target number of MPS molecules was varied from zero to 30 per nm^2 of silica surface area. This reaction was carried out at pH 8.5–9.0 for 5–6 h at 70 °C in each case. After centrifugal clean-up to remove excess unreacted MPS and alcohol by-product, contact angle goniometry studies were conducted on pressed pellets of MPS-modified silica particles to assess the extent of surface modification. At between 10 and 13 targeted MPS molecules per nm^2, the contact angle abruptly switches from less than 90° to more than 90°, which indicates that the silica particles have become hydrophobic (see **Figure 2**a). In principle, a more hydrophobic silica surface should promote more uniform PPy deposition but in practice highly hydrophobic silica particles are prone to aggregation in the aqueous solution required for PPy deposition (see below). Thus a target surface modification of 10 MPS molecules per nm^2 of silica was selected as a compromise for both the 1.0 μm and the 0.50 μm silica sols. Other target degrees of surface modification were also evaluated, but it was found empirically that targeting 10 MPS molecules per nm^2 of silica gave the most uniform PPy coatings.

Disk centrifuge photosedimentometry (DCP) is a high resolution particle sizing technique that can also be used to assess the degree of dispersion of colloidal particles.[5b,22] DCP studies

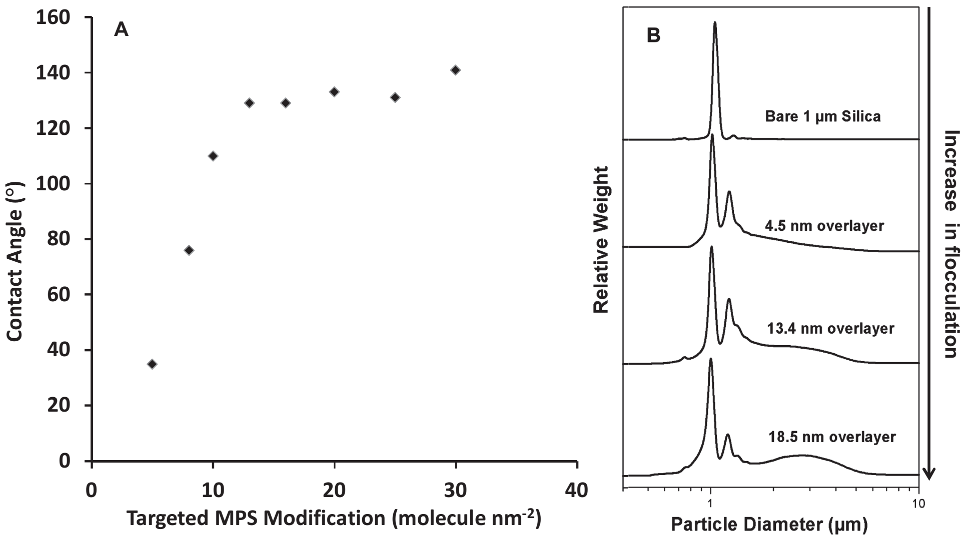

Figure 2. a) Contact angle measurements obtained for 1.0 µm silica sol with varying degrees of target surface modification using MPS. b) Disk centrifuge photosedimentometry (DCP) weight-average particle size distribution curves obtained for MPS-modified 1.0 µm silica particles with varying target degrees of surface modification. Prior to DCP analysis, these aqueous dispersions were subjected to ultrasonic treatment for 30 min.

of the two pristine silica sols indicate narrow size distributions, with weight-average diameters of 1.05 ± 0.08 µm and 0.46 ± 0.05 µm, respectively. These values are in reasonably good agreement with the nominal diameters provided by the silica sol manufacturer. Surface modification of these silica sols using increasing amounts of MPS eventually leads to incipient flocculation, as the particles become too hydrophobic to remain well-dispersed in aqueous solution. This aggregation can be conveniently monitored using DCP, see Figure 2b. The pristine aqueous 1.0 µm silica sol is well dispersed, with a major population of single particles and only a very minor population observed at higher diameter, which corresponds to doublets. Incipient flocculation is observed as higher degrees of MPS surface modification are targeted. However, for the 0.50 µm silica sol, the extent of aggregation due to surface modification indicated by DCP studies is rather more significant (see Figure S1, Supporting Information).

The results obtained for the PPy deposition experiments conducted using such MPS-modified 1.0 µm silica particles are summarized in **Table 1**. In these experiments, the silica sol concentration was fixed at 5.0 w/v% and the amounts of pyrrole monomer and oxidant were adjusted in order to vary the target PPy mass loading from zero to 8.1%. Assuming that (i) all of the pyrrole monomer is converted into PPy and (ii) the

Table 1. Summary of data obtained by preparing PPy-coated 1.0 µm silica particles, using a fixed target of 10 MPS molecules per nm^2 for the initial silica sol modification and a variable target PPy overlayer thickness (zero to 20 nm).

Entry	Targeted PPy mass loading [wt%]	Targeted PPy overlayer thickness [nm][a)]	PPy mass loading measured by TGA [wt%]	PPy overlayer thickness from TGA [nm][a)]	Nitrogen microanalysis content [%]	PPy mass loading from nitrogen microanalysis [wt%][b)]	PPy overlayer thickness from nitrogen microanalysis [nm][a)]	Four-point probe conductivity [S cm^{-1}][c)]	PPy surface coverage [%][d)]
1	0.0	0.0	0.0	0.0	0.00	0.0	0.0	$<10^{-6}$	N/A
2	0.4	1.0	0.2	0.4	0.02	0.1	0.3	$<10^{-6}$	N/D
3	1.1	2.5	1.1	2.5	0.18	1.1	2.5	$<10^{-6}$	10
4	2.1	5.0	2.0	4.8	0.30	1.9	4.5	$<10^{-6}$	29
5	3.1	7.5	2.8	6.8	0.47	2.9	7.0	$<10^{-6}$	35
6	4.2	10.1	3.7	8.9	0.74	4.6	11.1	$<10^{-6}$	51
7	5.0	12.2	4.4	10.6	0.89	5.5	13.4	$<10^{-6}$	55
8	6.1	14.9	4.9	11.9	0.92	5.7	13.9	4.0×10^{-3}	52
9	8.1	20.0	6.0	14.6	1.21	7.5	18.5	1.4×10^{-2}	60

[a)] Calculated using the equation derived by Lascelles and Armes;[6e] [b)] Calculated by comparing the nitrogen microanalytical contents of the PPy-coated silica particles to that of PPy bulk powder; [c)] Conducted on pressed pellets at 20 °C; [d)] Determined by X-ray photoelectron spectroscopy by comparing the N1s signal intensities of the PPy-coated silica particles to that of PPy bulk powder [N/A = not applicable; N/D = not determined].

conducting polymer is efficiently deposited onto the silica in the form of a thin uniform shell, this corresponds to a mean PPy overlayer thickness ranging from 0 to 20 nm. These thicknesses are comparable with those recorded previously by Armes and Lascelles when coating polystyrene latexes with PPy overlayers.[6h] In principle, the PPy mass loading can be determined using either thermogravimetry (TGA) or elemental microanalyses, using bare silica and PPy bulk powder as appropriate reference materials. As shown in Table 1, the mass loss observed when targeting a 20 nm PPy overlayer thickness is 6.0%, which is readily detectable using TGA. However, this technique suffers from two sources of experimental error. First, the MPS groups introduced via silane surface modification will also undergo pyrolysis in addition to the PPy component. Second, any surface moisture present will also make a contribution to the observed mass loss. In view of these systematic errors, elemental microanalysis is preferred for assessing the PPy mass loading on the silica particles, despite its lower sensitivity. For this technique, there is a choice of elements: carbon or nitrogen. The carbon content of PPy is significantly higher than its nitrogen content. However, the MPS surface groups will also make a contribution to the former element, so the latter element is preferred in this context, even though it is subject to a larger experimental error ($N = \pm 0.20\%$). Inspecting Table 1, there is a reasonably good correlation between each targeted PPy mass loading and those indicated by nitrogen microanalysis. This indicates that both the pyrrole polymerization and the PPy deposition are quite efficient under the chosen reaction conditions. Similar observations have been reported by Lascelles and Armes for PPy deposition onto micrometer-sized polystyrene latexes.[6d,e,h] This suggests that the extent of surface modification achieved using a targeted 10 MPS molecules per nm^2 is sufficient to promote deposition. For relatively low PPy mass loadings, no measurable conductivities could be determined for pressed pellets prepared from PPy-coated 1.0 μm silica particles. However, for PPy mass loadings of 5.7% and 7.5%, conductivities of 4.0×10^{-3} and 1.4×10^{-2} S cm^{-1} were determined using the four-point probe method (see penultimate column in Table 1). These values are much higher than that of pristine silica (≈10^{-8} S cm^{-1}), but somewhat lower than the conductivity of PPy bulk powder (>1 S cm^{-1}).[2c] It is also noteworthy that higher conductivities (0.5 S cm^{-1}) have been achieved for PPy-coated polystyrene latexes at comparable PPy mass loadings.[6e] As we shall see, this difference is most likely attributable to differences in the surface morphology of the PPy overlayer.

XPS is a highly surface-specific characterization technique with a typical sampling depth of 2–10 nm. As described by Perruchot and co-workers, it can be utilized to assess the surface coverage of PPy overlayers on colloidal substrates.[23] For the present system, XPS studies confirm that no nitrogen species can be detected at the surface of the pristine silica sols (see Figure S2, Supporting Information). Thus nitrogen acts as a unique elemental marker for the PPy component. Hence the intensity of the XPS N1s signal at around 400 eV observed for the various PPy-coated silica samples can be simply compared to that of PPy bulk powder (see final column in Table 1). This convenient approach indicates that PPy surface coverages of 50–60% can be achieved, which is somewhat lower than the surface coverage of 94–100% observed for PPy overlayers deposited onto a micrometer-sized polystyrene latex.[23] This difference is consistent with the lower conductivities observed for the PPy-coated silica particles.

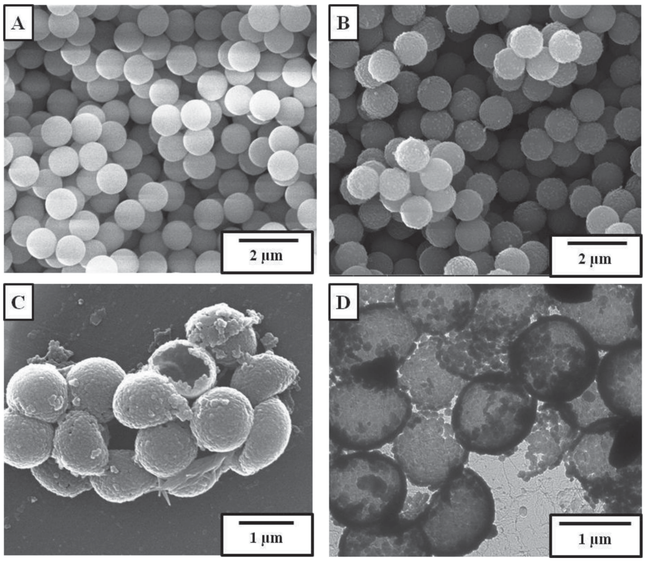

Figure 3. SEM images obtained for a) 1.0 μm pristine silica sol, b) 1.0 μm MPS-modified silica (target degree of surface modification = 10 MPS molecules per nm^2) with PPy mass loading of 5.0% (see entry 7 in Table 1), c) the same 1.0 μm PPy-coated silica after etching with excess HF to remove the silica cores. d) TEM image of the sample shown in (c).

A typical SEM image recorded for the 1.0 μm silica sol is shown in **Figure 3**a. These particles are spherical, near-monodisperse and have a relatively smooth surface. The mean number-average diameter is approximately 1.05 μm, which is in fairly good agreement with the manufacturer's nominal diameter. Figure 3b shows the same silica sol after MPS surface modification (target 10 MPS per nm^2 of silica sol), followed by PPy deposition when targeting a PPy mass loading of 5.0% (see entry 7 in Table 1). There is a distinct change in the surface morphology, with clear evidence for a fairly uniform, albeit somewhat globular, PPy overlayer. After treatment with excess HF to remove the underlying silica cores, some of residual PPy shells become ruptured and reveal their hollow nature, see Figure 3c. This observation is also consistent with TEM analysis of the same HF-etched particles, which indicates cores of relatively low contrast (see Figure 3d). Thus these electron microscopy studies confirm the well-defined core–shell nature of the original hybrid particles.[24] Close inspection of the TEM image shown in Figure 2d suggests a characteristic PPy globule diameter of 50–100 nm. This is significantly greater than the minimum PPy grain size of 5–10 nm indicated by SEM studies of a range of PPy samples.[25]

Hence it appears that the PPy actually deposits onto the MPS-modified silica particles in the form of relatively coarse colloidal particles whose dimensions significantly exceed the maximum targeted overlayer thickness of 20 nm, see Table 1. This is of course consistent with the XPS studies, which indicate substantially incomplete surface coverage, as expected for

Table 2. Summary of data obtained by preparing PPy-coated 0.50 μm silica particles, using a fixed target of 10 MPS molecules per nm^2 for the initial silica sol modification and a variable target PPy overlayer thickness (zero to 20 nm).

Entry	Targeted PPy mass loading [wt%]	Targeted PPy overlayer thickness [nm]$^{a)}$	PPy mass loading measured by TGA [wt%]	PPy overlayer thickness from TGA [nm]$^{a)}$	Nitrogen microanalysis content [%]	PPy mass loading from nitrogen microanalysis [wt%]$^{b)}$	PPy overlayer thickness from nitrogen microanalysis [nm]$^{a)}$	Four-point probe conductivity [S cm^{-1}]$^{c)}$	PPy surface coverage [%]$^{d)}$
1	0.0	0.0	0.0	0.0	0.00	0.0	0.0	$<10^{-6}$	N/A
2	2.3	2.5	2.3	2.4	0.28	1.7	1.9	$<10^{-6}$	25
3	4.6	5.0	4.5	4.9	0.67	4.2	4.5	$<10^{-6}$	N/D
4	6.8	7.5	5.2	5.7	0.82	5.1	5.6	$<10^{-6}$	20
5	9.0	10.1	6.0	6.6	0.93	5.8	6.4	$<10^{-6}$	N/D
6	11.0	12.5	11.4	13.0	1.79	11.1	12.6	1.5×10^{-2}	38
7	13.1	15.0	11.1	12.6	1.87	11.6	13.2	5.1×10^{-2}	N/D
8	17.0	20.0	15.0	17.4	2.51	15.6	18.2	4.6×10^{-1}	61

$^{a)}$Calculated using equation derived by Lascelles and Armes;[6e] $^{b)}$Calculated by comparing the nitrogen microanalytical contents of the PPy-coated silica particles to that of PPy bulk powder; $^{c)}$Conducted on pressed pellets at 20 °C; $^{d)}$Determined by x-ray photoelectron spectroscopy by comparing the N1s signal intensities of the PPy-coated silica particles to that of PPy bulk powder [N/A = not applicable; N/D = not determined].

pseudo-spherical PPy particles inefficiently packed at the surface of a large silica sphere.

Similar electron microscopy observations were made for the PPy-coated 0.50 μm silica particles (see Figure S3, Supporting Information). Again, the pristine silica sol had a rather featureless surface morphology and a relatively narrow size distribution, with a mean number-average diameter of around 0.46 μm. This smaller silica diameter leads to a somewhat rougher surface texture, perhaps in part because its dimensions are more comparable to that of the deposited PPy globules. However, we also attribute this reduced morphological control to the less uniform nature of the PPy deposition that is achieved in this case. This is most likely because we chose to work at a fixed silica concentration when coating both the 0.50 μm and the 1.0 μm silica particles. Thus the smaller silica particles have twice the available surface area, so twice as much pyrrole and oxidant are required in the PPy coating formulation to achieve the same PPy overlayer thickness. These higher reagent concentrations have the effect of increasing the rate of PPy formation in aqueous solution, which leads to poorer control over the deposition process.

Moreover, the smaller silica core dimensions also lead to significantly higher PPy mass loadings for a given target PPy overlayer thickness. For example, targeting a 20 nm PPy overlayer now requires a target PPy mass loading of 17%. This leads to improved accuracy in the experimental determination of the actual PPy mass loadings using TGA and nitrogen microanalyses, see **Table 2**. In general, similar trends are observed for the 0.50 μm silica sol as those found for the 1.0 μm silica sol: PPy deposition is relatively efficient and there is a good correlation between the target and actual mass loadings. Measurable conductivities are only obtained at a PPy mass loading of 11%, which corresponds to an apparent overlayer thickness of 12.5 nm. Slightly higher conductivities (up to 0.46 S cm^{-1}) and XPS surface coverages (up to 61%) can be achieved in this case.

Further HF etching experiments were conducted on PPy-coated 1.0 μm silica particles to assess the nature of the PPy overlayer with increasing surface coverage (see **Figure 4**). The resulting PPy residues were examined by TEM in each case. At a PPy mass loading of 1.9% (see entry 4 in Table 1), the conducting polymer overlayer is clearly non-contiguous, since no PPy shells remain intact after HF removal of the underlying silica cores, see Figure 4a. At a PPy mass loading of 5.5% (see entry 7 in Table 1), some PPy shells are observed, but others have disintegrated. Finally, at a PPy mass loading of 7.5% (see entry 9 in Table 1), discrete PPy shells are observed, which indicates that a contiguous PPy overlayer was formed under these synthesis conditions. These observations are remarkably consistent with the pressed pellet conductivities in Table 1: measurable conductivities are only observed at a PPy mass loading of 7.5% since contiguous conductive shells are a prerequisite for efficient macroscopic charge transport.[6e]

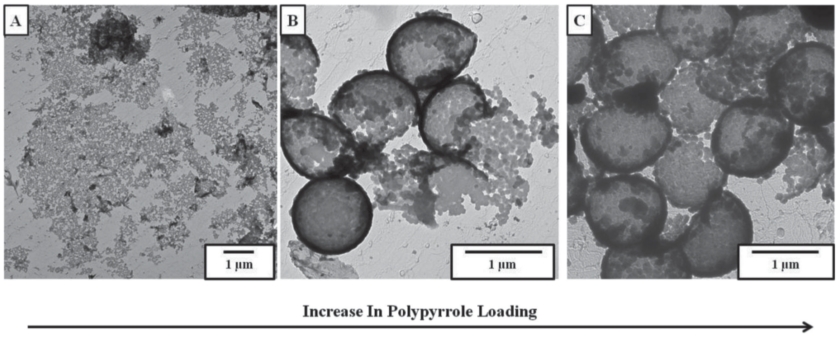

Figure 4. TEM images obtained of HF-etched PPy-coated 1.0 μm silica particles prepared with various PPy mass loadings a) 1.9% equivalent to a PPy overlayer thickness of 4.5 nm (see entry 4 in Table 1), b) 5.5% equivalent to a PPy overlayer thickness of 13.4 nm (see entry 7 in Table 1), c) 7.5% equivalent to a PPy overlayer thickness of 18.5 nm (see entry 9 in Table 1). Note PPy mass loadings have been calculated using microanalysis.

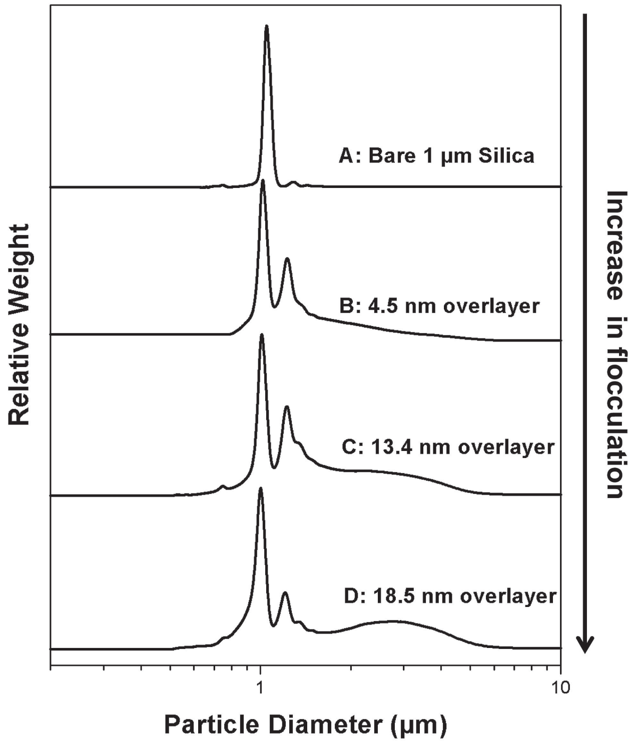

Figure 5. DCP traces obtained from a) 1.0 µm silica sol (see entry 1 Table 1) and PPy-coated 1.0 µm silica particles prepared with various PPy mass loadings b) 1.9% equivalent to a PPy overlayer thickness of 4.5 nm (see entry 4 in Table 1), c) 5.5% equivalent to a PPy overlayer thickness of 13.4 nm (see entry 7 in Table 1), d) 7.5% equivalent to a PPy overlayer thickness of 18.5 nm (see entry 9 in Table 1). Note PPy mass loadings have been calculated using microanalysis. Prior to DCP analysis, these aqueous dispersions were subjected to ultrasonic treatment for 30 min.

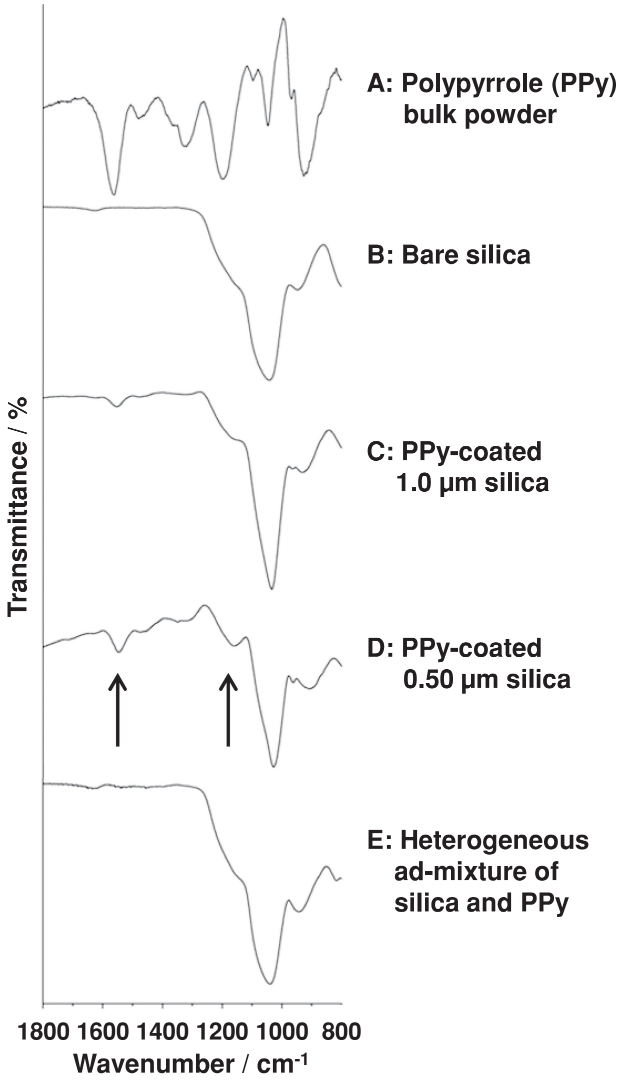

Figure 6. FT-IR spectra recorded for: a) PPy bulk powder prepared using $FeCl_3$ oxidant, b) pristine 1.0 µm silica (see entry 1 in Table 1), c) PPy-coated 1.0 µm silica particles with a PPy mass loading of 7.5% equivalent to an overlayer thickness of 18.5 nm (see entry 9 in Table 1), d) PPy-coated 0.50 µm silica particles with a PPy mass loading of 15.6% equivalent to an overlayer thickness of 18.2 nm (see entry 8 in Table 2), and e) heterogeneous ad-mixture of 12 wt% PPy bulk powder with 1.0 µm silica particles.

Coating the MPS-modified 1.0 µm silica particles with a PPy overlayer has a detrimental effect on their colloidal stability, as judged by DCP. The PPy overlayer causes a significant increase in flocculation, see **Figure 5**. This is perhaps not surprising given the relatively high Hamaker constant of the PPy overlayer.[26] Moreover, similar observations have been recorded for PPy-coated polystyrene latexes.[6e,g] Even greater aggregation is observed when coating MPS-modified 0.50 µm silica particles with PPy (see Figure S4, Supporting Information). Presumably, this is related to the less uniform deposition achieved for this system (see above).

Fourier tranform infrared (FT-IR) spectra recorded for PPy bulk powder, pristine 1.0 µm silica particles, PPy-coated 1.0 µm silica particles, PPy-coated 0.50 µm silica particles and a heterogeneous ad-mixture of PPy plus 1.0 µm silica are shown in **Figure 6**. This spectroscopic technique can be used to confirm the presence of high-quality, electrically conductive PPy chains adsorbed on the silica particles. The bands observed at approximately 1550, 1300, and 1150 cm^{-1} in Figure 6a are characteristic of doped PPy,[5b] whereas the intense broad band centred at 1050 cm^{-1} in Figure 6b is assigned to the Si–O stretch that is characteristic of silica. The spectra recorded for the 1.0 µm and 0.50 µm PPy-coated silica particles (see Figures 6c,d) are quite similar to that obtained for the pristine silica sol. However, additional PPy bands are observed at 1550, 1300, and 1150 cm^{-1} (as indicated by the two arrows), confirming the presence of this organic component. Such bands are more intense for the 0.50 µm PPy-coated silica particles, since this sample contains a rather higher PPy mass loading. Moreover, the relative intensities of these PPy bands are significantly weaker in the spectrum recorded for the heterogeneous ad-mixture (see Figure 6e), even though this latter sample contains almost twice as much PPy by mass (12 wt%) as the 1.0 µm PPy-coated silica particles (Figure 6c). This indicates enhanced PPy band intensities arising from the core–shell nature of the PPy-coated silica particles. Similar FT-IR observations were reported

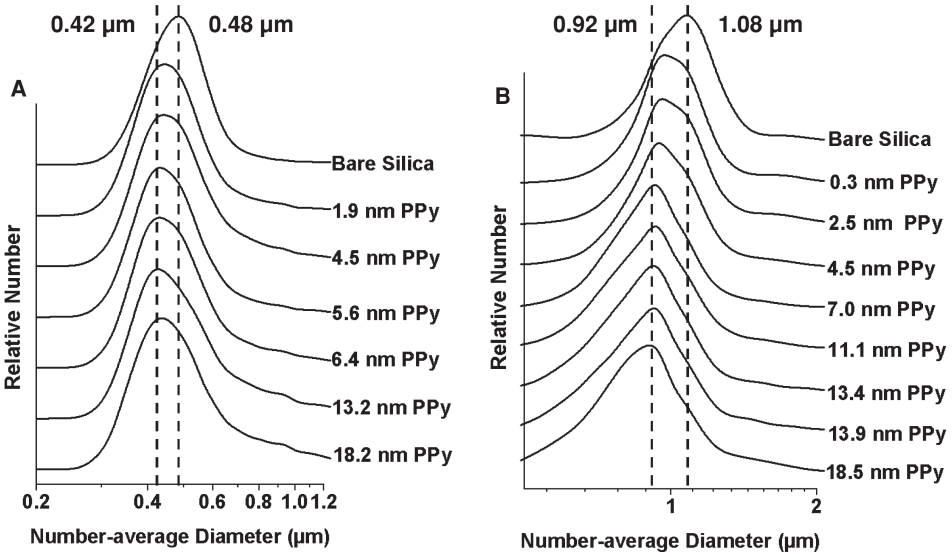

Figure 7. Aerosol particle size distributions obtained for a) 0.50 µm PPy-coated silica particles and b) 1.0 µm PPy-coated silica particles of varying PPy overlayer thickness using a white light aerosol spectrometer (WELAS). See Tables 1, 2 for sample details.

by Lascelles and Armes for PPy-coated micrometer-sized polystyrene latex particles.[6e]

When the oven-dried PPy-coated silica particles were subjected to white light aerosol spectrometry (WELAS) analysis in the gas phase, a relatively high degree of dispersion was observed (see **Figure 7**). Since the pristine silica particles do not readily disperse as a "smoke", this is likely to be due to the highly cationic nature of the PPy overlayer: strong electrostatic repulsion between adjacent particles results in the formation of a spontaneous and relatively long-lasting aerosol after minimal agitation of dry PPy-coated silica particles.[10a] However, close inspection of the data shown in Figure 7 reveals that the WELAS technique suffers from an interesting experimental artefact: the apparent diameter of the PPy-coated silica particles appears to decrease at higher PPy loadings. Even if the PPy coating causes no particle clumping, a small increase in mean particle size might be anticipated because of the thickness of the PPy overlayer. That the apparent reduction in aerosol dimensions is indeed an artefact was confirmed by removing the PPy overlayer using excess sodium hypochlorite,[27] which digests the PPy chains but does not degrade the underlying silica. As expected, the silica particles recovered after this oxidative bleach treatment are identical in size to the pristine silica sol, as judged by DCP analysis (see Figure S5, Supporting Information). Thus, the PPy deposition protocol (which is conducted at low pH) does not result in any significant in situ dissolution of the silica particles. Hence, the apparent undersizing observed in the WELAS experiments shown in Figure 7 is undoubtedly the result of a systematic error. The most likely explanation for this experimental artefact is the use of an incorrect particle refractive index, which is an input parameter for the WELAS measurements. The refractive index for silica was used for all measurements. This is appropriate for the pristine white silica sol, but clearly it is inappropriate for the PPy-coated silica particles, which range in color from light grey to dark grey/black depending on the PPy mass loading. The WELAS instrument determines particle size from the amount of scattered light according to Mie theory, with larger particles scattering light much more strongly. However, the highly absorbing (black) PPy overlayer has an imaginary refractive index and hence interacts with light very differently to (white) silica, which has no imaginary component. Since PPy is highly absorbing across the whole visible light spectrum, much less light is scattered from PPy-coated silica particles than for purely reflective silica particles of equivalent size. The WELAS instrument incorrectly perceives this reduction in light scattering as indicating the presence of smaller particles, which leads to the sizing artefact shown in Figure 7. This interpretation also explains why there is a systematic shift to smaller particle diameters at higher PPy loadings for the 1 µm silica particles, since particles coated in thicker PPy overlayers will absorb visible light more strongly (it is not clear why there is little or no discernible systematic shift observed for the 0.50 µm silica particles, but it is perhaps noteworthy that the latter particles are close to the lower size limit of 0.20 µm for the WELAS instrument). Despite the sizing artefact indicated in Figure 7, it is nevertheless clear that these WELAS measurements provide strong evidence for a high degree of dispersion of the PPy-coated silica particles in the gas phase. Moreover, such WELAS-determined aerosol size distributions are arguably more relevant than the DCP data for predicting the behavior of these PPy-coated silica particles in van de Graaff experiments for space science experiments.

So-called 'black carbon' is a well-documented particulate airborne pollutant produced by the incomplete combustion of organic material.[28] For example, one primary source of black carbon is automotive diesel soot. This man-made atmospheric species has been recently implicated as being second in importance only to carbon dioxide in the context of global warming.[28a] According to the literature, black carbon is likely to be responsible for significant changes in regional weather patterns in

India and China.[29] Thus the detection and quantification of black carbon in the Earth's atmosphere is currently the focus of extensive environmental research.[30] However, such studies are somewhat problematic in view of the complex morphology and broad size distribution of black carbon particles.[31] Moreover, refractive index measurements on black carbon have proved to be rather controversial, with experimental discrepancies being reported by various teams.[31,32] Clearly, the availability of a highly absorbing model aerosol comprising near-monodisperse spherical particles should play an important role in clarifying the basic optical physics of black carbon. We suggest that the micrometer-sized polypyrrole-coated silica particles described herein may be useful in this context, particularly given that systematic variation of the polypyrrole loading should allow modulation of the light absorption behavior of these model aerosols. We intend to explore this application in future work.

3. Conclusions

In summary, colloidal silica particles can be readily surface modified with MPS and subsequently coated with PPy via a convenient one-pot aqueous formulation. Contact angle goniometry studies on pressed pellets indicate that the optimum target degree of surface modification is around 10 MPS per nm^2 of silica surface area; these conditions produce a contact angle of around 110°. This silanization protocol renders the 1.0 μm silica particles sufficiently hydrophobic to allow efficient PPy deposition from aqueous solution, without unduly compromising their colloidal stability. Electron microscopy studies confirm that the PPy is deposited onto the silica particles in the form of 50–100 nm globules to form a particulate overlayer. Non-contiguous overlayers are obtained at low PPy mass loadings, while contiguous overlayers are obtained at high PPy mass loadings; the latter is a pre-requisite for measurable electrical conductivities using the four-point probe method on pressed pellets. As expected, the FT-IR spectrum of the PPy-coated silica particles is dominated by the silica core, since this is the major component. Nevertheless, it is also possible to observe several bands that are characteristic of the doped PPy component. Targeting higher PPy mass loadings leads to a significant increase in the degree of flocculation of PPy-coated silica particles in aqueous solution as judged by DCP, since the relatively high Hamaker constant of the conducting polymer overlayer leads to greater inter-particle interactions. However, using an established aerosol sizing technique (WELAS), it was found that the dried PPy-coated silica particles exhibit a surprisingly high degree of dispersion in the gas phase, presumably due to strong electrostatic repulsion between the cationic PPy overlayers. In these WELAS studies, increasing the PPy mass loading leads to an apparent reduction in particle size. Given the highly absorbing nature of the PPy overlayer, this artefact most likely arises from the deployment of inappropriate refractive index data. This hypothesis is supported by the observation that removal of the PPy coating using excess sodium hypochlorite allows the recovery of silica particles that are identical in size to that of the original pristine silica sols, as judged by DCP. The PPy-coated silica particles described herein are currently being evaluated as synthetic mimics for inorganic micrometeorites in Van der Graaf accelerator experiments. In this context, the electrically conductive PPy overlayer is critical for the efficient acceleration of such particles up to the hypervelocity regime, since it allows accumulation of substantial surface charge. Given the growing environmental interest in diesel soot particulates as atmospheric pollutants, it is also likely that these highly absorbing near-monodisperse aerosols may serve as useful calibrants for aerosol sizing instruments.

4. Experimental Section

Materials: Low polydispersity silica particles with nominal manufacturer diameters of 1.0 μm and 0.50 μm were purchased from Blue Helix (UK) and were used as received. BET surface area measurements (Quantachrome Nova 1000e instrument) indicated specific surface areas of 3.3 and 9.4 m^2 g^{-1} respectively, which suggests some degree of micro-porosity. 3-(Trimethoxysilyl)propyl methacrylate (MPS; purity 98%), pyrrole and $FeCl_3.6H_2O$ were obtained from Sigma-Aldrich (UK). Pyrrole was purified using basic alumina chromatography prior to polymerization. All other chemicals were obtained from Sigma-Aldrich and used as received. Deionized water was used in all experiments.

Preparation of Polypyrrole Bulk Powder Using $FeCl_3$: $FeCl_3.6H_2O$ (9.10 g, 33.7 mmol) was dissolved in deionized water (100 g). Under continuous stirring, pyrrole monomer (1.0 mL, 14.4 mmol) was added to the reaction mixture using a micropipet. The reaction was stirred for 24 h at 20 °C. A color change from orange to green to black was observed as PPy precipitate was formed. The precipitate was vacuum-filtered using a Buchner funnel and washed thoroughly with first deionized water and then methanol. The purified black PPy powder was dried in a vacuum oven at 40 °C overnight. The purified product was analyzed by elemental analysis and yields of 90–95% were typically achieved under these conditions.

Preparation of 3-(Trimethoxysilyl)propyl Methacrylate-Modified Silica Particles: Silica (1.0 μm nominal diameter; 1.00 g, 16.6 mmol) was dispersed in deionized water (4.0 g) as a 20 wt% solution. NH_4OH (0.1 m) was added dropwise to adjust the pH of the dispersion to pH 8.5–9.0. This silica dispersion was heated to 70 °C and MPS (11.5 μL, 0.048 mmol; 10 MPS per nm^2 of silica particles) was added using a micropipet. The dispersion was stirred vigorously for 5–6 h before being cooled to 20 °C. The MPS-modified silica particles were purified by three centrifugation-redispersion cycles (at 3500 rpm for 30 min). After each cycle, the supernatant was carefully removed and the particles were redispersed in deionized water. The purified particles were dried overnight in an oven at 40 °C under reduced pressure.

One-Pot Preparation of Polypyrrole-Coated Silica Particles Using 3-(Trimethoxysilyl)propyl Methacrylate: A typical one-pot polypyrrole coating protocol was conducted as follows. 1.0 μm silica (1.00 g, 16.6 mmol) was dispersed in deionized water (4.0 g) as a 20 wt% solution. NH_4OH (0.1 m) was added dropwise to the dispersion until pH 8.5–9.0 was obtained. This silica dispersion was heated to 70 °C and MPS (11.5 μL, 0.048 mmol; 10 MPS per nm^2 of silica particles) was added using a micropipet. The dispersion was stirred vigorously for 5–6 h before being cooled to 20 °C. Under continuous stirring, additional deionized water was added to the MPS-modified silica particles to form a 5 wt% solution. The MPS-modified silica particles were coated in PPy by first dissolving $FeCl_3.6H_2O$ (0.41 g, 1.52 mmol) in the dispersion to give an orange-colored solution. Pyrrole (45 μL, 0.65 mmol) was added to the dispersion using a micropipet and stirred for 24 h. A color change from orange to green to black was observed and a black dispersion of PPy-coated silica particles was obtained. The particles were purified by three centrifugation-redispersion cycles (3500 rpm for 30 min). After each cycle, the supernatant was carefully removed and the particles were redispersed in deionized water (in order to remove spent oxidant and other impurities such as unreacted MPS and alcohol by-product). The purified particles were dried overnight in an oven at 40 °C under reduced pressure and were then analyzed by elemental microanalysis. This protocol was adjusted by varying the target degree of MPS modification and target PPy overlayer thickness. The latter was achieved by varying the mass of the pyrrole monomer and oxidant, while maintaining a fixed silica mass. The PPy mass fraction required to give this thickness was calculated using the equation reported by Lascelles and Armes.[6e] Assuming that the PPy overlayer is both smooth and uniform, the corresponding mean PPy overlayer thicknesses can be readily calculated from the mean radius of the silica core particles, the densities of the silica and PPy and the respective mass fractions of these two components.

Helium Pycnometry: The solid-state densities of the bare silica, MPS-modified silica, 0.50 and 1.0 μm PPy-coated silica particles and PPy bulk powder were determined at 20 °C using a helium pycnometer (Micromeritics AccuPyc 1330 instrument). All samples were dried under vacuum prior to analysis.

Scanning Electron Microscopy: Images were obtained using a FEI Inspect SEM instrument operating at 20 kV. Prior to examination, the samples were sputter-coated with gold to prevent sample charging effects.

Disk Centrifuge Photosedimentometry: Disk centrifuge photosedimentometry (DCP) particle size analysis was conducted using a CPS centrifuge DC24000 instrument operating in "line start" mode at 3500 rpm, and the spin fluid comprised a density gradient built up from 8.0 to 24.0 wt% aqueous sucrose solutions; a small volume of *n*-dodecane (0.50 mL) was used to extend the lifetime of this gradient.

White Light Aerosol Spectrometry: WELAS particle size analysis was conducted using a WELAS digital 3000 instrument at Particle Technology Ltd. (Hatton, Derbyshire, UK). Approximately 0.50 g of vacuum oven-dried particles were placed on a disk feeder which allowed a continuous flow of particles to be dispersed in air. A venture valve aids particle dispersal by allowing the simultaneous operation of compressed air and vacuum. Aggregated particles are further dispersed by impinging onto a metal plate to break up agglomerates prior to analysis. The dispersed airborne particles enter the detection chamber where they scatter photons from an incident white light source. The scattered light is detected at 90° and typically 2×10^5 particles can be analyzed within 60 s. The mean aerosol size is reported as a number-average diameter. Prior to sample analysis, the WELAS instrument was calibrated using a well-defined silica sol (PALAS Caldust 1100). According to SEM analysis, this calibration standard had a number-average diameter of 1080 ± 30 nm (200 particles counted). In these aerosol sizing experiments, the particle density of each sample was taken to be 2.0 g cm^{-3} and the particle refractive index was taken to be that of silica (1.54).

Contact Angle Measurements: 10 mm diameter pellets of the surface-modified silica particles were prepared using a pellet press operating under vacuum at a pressure of 9 kg cm^{-2}. The contact angles of MPS-modified silica particles were measured using a contact angle goniometer by placing a 10 μL droplet of deionized water onto pressed pellets at 20 °C.

Elemental Analysis: Approximately 10 mg of each dried sample was analyzed by the Elemental Analysis Service Laboratory within the Department of Chemistry at the University of Sheffield, UK using a Perkin Elmer 2400 instrument.

Conductivity Measurements: A conventional four-point probe set-up was used to measure the conductivities of pressed pellets of PPy-coated silica particles at 20 °C. The lower limit conductivity that can be determined with this set-up is approximately 10^{-6} S cm^{-1}.

Fourier Transform Infra-Red Spectroscopy: FT-IR spectra were recorded using a Thermo Scientific Nicolet IS10 spectrometer. Vacuum oven-dried samples were analyzed using a Diamond ATR 'Golden Gate' accessory. Each spectrum was averaged over 32 scans at a resolution of 4 cm^{-1}.

X-Ray Photoelectron Spectroscopy: Selected dried powders (pristine silica, MPS-modified silica particles, PPy-coated silica particles and PPy bulk powder) were analyzed by X-ray photoelectron spectroscopy (XPS) using a Kratos Axis Ultra DLD X-ray photoelectron spectrometer equipped with a monochromatic Al X-ray source operating at 6.0 mA and 15 kV at a typical base pressure of 10^{-8} Torr. The step size was 0.5 eV for the survey spectra (pass energy = 160 eV) and 0.05 eV for the high resolution spectra (pass energy = 80 eV). Spectra were typically acquired from at least two separate sample areas.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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