Synthesis and characterization of monodisperse silica–polyaniline core–shell nanoparticles

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Monodisperse silica–polyaniline core–shell nanoparticles with an average diameter of 26 nm were synthesized by *in-situ* polymerisation of aniline monomers adsorbed on the silica surface through electrostatic interactions.

There has been tremendous interest in the fabrication of polymer-coated core–shell nanoparticles with unique and tailored properties for various applications.[1] These composite nanoparticles provide a robust platform for incorporating processability and diverse functionalities from the polymer into a single particle. To date, a number of methods have been described for generating organic polymer shells on inorganic cores, which include surface polymerization from particle-bound initiators,[2] layer-by-layer deposition,[3] crosslinking of polymeric micelles surrounding the inorganic cores,[4] and vapor deposition polymerization.[5] In the coating of inorganic particles with polymer shells, the specific chemical interaction between the particle surface and the polymer surrounding the core must be tailored in order to form a uniform shell.

Among the various core–shell nanoparticles, the preparation of silica nanoparticles coated by a thin layer of conducting polymers is of particular interest, because the surface of the nanoparticles can easily be altered to accommodate specific catalytic, magnetic, electronic, optical, or optoelectronic properties. In addition, these core–shell nanoparticles combine the properties of the conducting polymer shells and the high colloidal stability of the silica cores, which could greatly widen their applicability in fields of catalysis, electronics, and optics. Polyaniline (PANI) is one of the most technologically promising conducting polymers due to its ease of synthesis, low cost, unique redox behavior, environmental and chemical stability, and relatively high conductivity.[6] Although several methods have been reported for the synthesis of micrometer-sized PANI-coated polymeric latex particles[7] or silica spheres,[8] coating of silica nanoparticles with PANI is still challenging and a more simple alternative method is desired.

In this work, a facile approach has been developed for the fabrication of silica–PANI core–shell nanoparticles less than 30 nm in diameter. The PANI shell was formed by *in-situ* polymerization of positively charged anilinium ions adsorbed on the negatively charged surface of the silica nanoparticle through electrostatic interactions. The silica cores serve as templates for adsorption of aniline monomers as well as counter-ions for doping of the synthesized PANI. This process is simple (one-step), environmentally benign, and results in the formation of a uniform PANI layer

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as thin as 2 nm on the surface of silica nanoparticles as small as 22 nm in diameter. This simple approach could provide an opportunity to design novel core–shell nanostructures with diverse functionality and high colloidal stability.

The overall synthetic procedure is represented in Scheme 1. In this approach, aniline monomers are converted to cationic anilinium ions in acidic conditions with a pH of 3 and adsorbed onto the negatively charged silica surface. Since aniline has a known pK_a of 4.63, it is expected to be primarily positively charged at pHs below this value. On the other hand, the silica nanoparticles possess negative charges on their surfaces at pHs greater than 2, *i.e.* the isoelectric point of silica. The aniline monomers electrostatically complexed to the silica surface were then polymerized by ammonium persulfate (APS) as an oxidizing agent at room temperature.

In a typical synthesis, Ludox TM-40 silica solution was used as a source for silica nanoparticles with an average diameter of 22 nm. Aniline monomer (0.2 g) was added to distilled water (50 mL) containing silica nanoparticles (0.8 g). An aqueous HCl solution (35 wt%) was added dropwise to the above-prepared solution until the pH of the solution was 3, and stirred for 1 h under vigorous stirring. APS (0.26 g), dissolved in distilled water (2 mL), was added to the aniline/silica solution. The polymerization of aniline was carried out at room temperature for 12 h. After the polymerization, a dispersion solution of the silica–PANI core–shell nanoparticles was obtained by centrifugation and re-dispersion of the nanoparticles in distilled water. In case of UV-vis measurements, the pH of the nanoparticle solution was adjusted by adding varying amounts of 1 M NaOH solution.

The polymerization of aniline was investigated by Fourier transform infrared (FT-IR) analysis. The characteristic peak of the silica–PANI core–shell nanoparticles appeared at 1582, 1484, and 1310 cm^{-1}, due to quinone ring deformation, benzene ring deformation, and C–N stretching of a secondary aromatic amine,
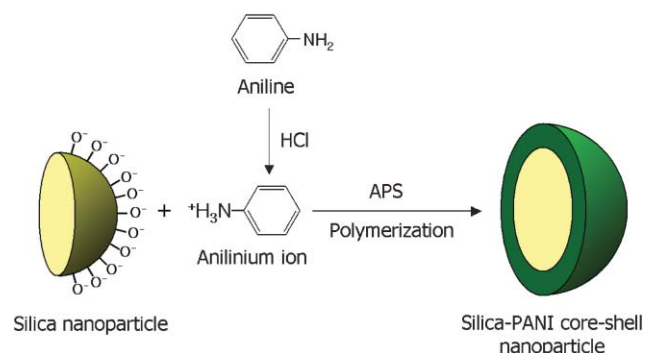
Scheme 1 Synthetic procedure of silica–PANI core–shell nanoparticles.

respectively.[9] This result demonstrates the successful polymerization of PANI onto the surface of the silica nanoparticles. The morphologies of the silica and silica–PANI core–shell nanoparticles were confirmed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) analyses. The SEM image of the silica nanoparticles dried from water showed that the particles were significantly agglomerated after drying (Fig. 1a). On the other hand, the silica–PANI core–shell nanoparticles existed as single particles and also retained the spherical shape of the particles (Fig. 1b). These results mean that thin PANI layers on the silica particle surfaces efficiently prohibited the agglomeration of the particles. The TEM observation revealed that the silica–PANI core–shell nanoparticles were nearly monodisperse and well dispersed in the TEM grid (Fig. 2). The outer shell of the particle exhibited a fine increment in brightness compared with the dark inner core, which confirmed the core–shell structure of the silica–PANI nanoparticles.

The ζ-potential of the silica nanoparticles measured at pH 3 showed a negative value (-50.3 mV) due to the negatively charged –OH groups on the silica particle surfaces. For the silica–PANI core–shell nanoparticles, the ζ-potential value was -1.3 mV, indicating that a sufficient number of negatively charged sites on the silica surfaces were neutralized by the PANI shells. These results also demonstrate the formation of the core–shell structure in that the silica–PANI behaves as one system rather than two separate species. The particle-size distribution for the silica–PANI core–shell nanoparticles was measured by dynamic light-scattering measurements (Fig. 3). The silica nanoparticles exhibited a particle size distribution centered at 22.3 nm in diameter. After coating with the PANI shell, the center of the particle size distribution moved from 22.3 to 26.2 nm, indicating that the shell thickness of PANI was about 2 nm.
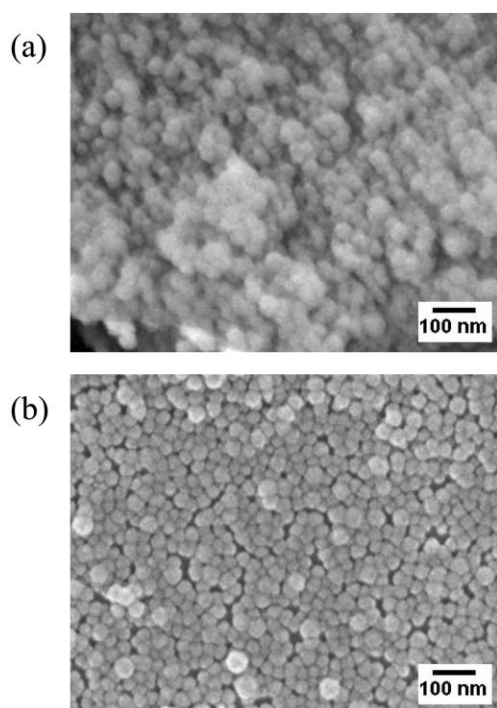

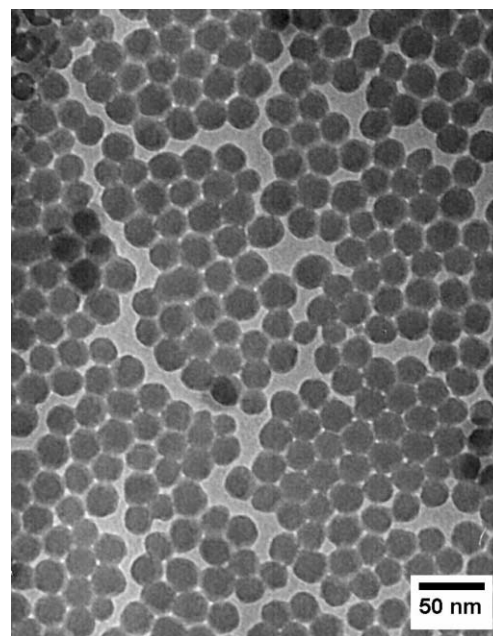**Fig. 1** SEM images of a) silica and b) silica–PANI core–shell nanoparticles.

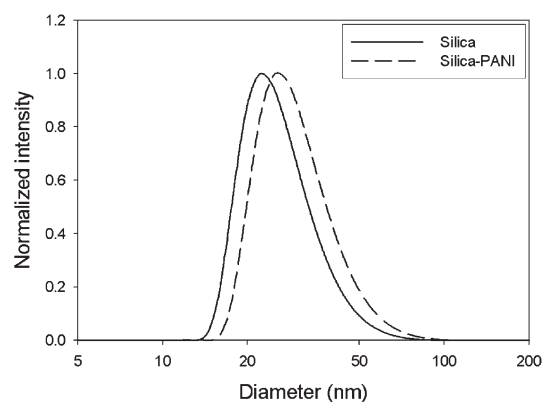**Fig. 2** TEM image of silica–PANI core–shell nanoparticles.

Fig. 3 Semilogarithmic plot of the particle size distribution curves of silica nanoparticles (solid line) and silica–PANI core–shell nanoparticles (dashed line) in a colloidal solution, determined by dynamic light scattering.

To investigate the reversible redox behavior of the silica–PANI core–shell nanoparticles, UV-vis absorption analysis was conducted with varying pH of the dispersion solution of the core–shell nanoparticles. Fig. 4a represents the UV-vis absorption spectra of the silica–PANI core–shell nanoparticles with increasing pH from 3 to 12. At pH 3, the PANI in the silica–PANI core–shell nanoparticles was in the doped state (emeraldine salt form of PANI) as reflected by the presence of the polaron band transition at about 420 and 800–1000 nm, as well as the π–π* transition of the benzenoid rings at about 310–320 nm.[10] As the pH of the solution increased up to 12, the polaron bands at 420 and 800–1000 nm gradually disappeared, and a strong absorption band at 600 nm emerged. The absorption band at 600 nm is attributed to the excitation from the HOMO (highest occupied molecular orbital, π_b) of the three-ring benzenoid part of the system to the LUMO (lowest unoccupied molecular orbital, π_q) of the localized quinoid ring and the two surrounding imine nitrogens in the
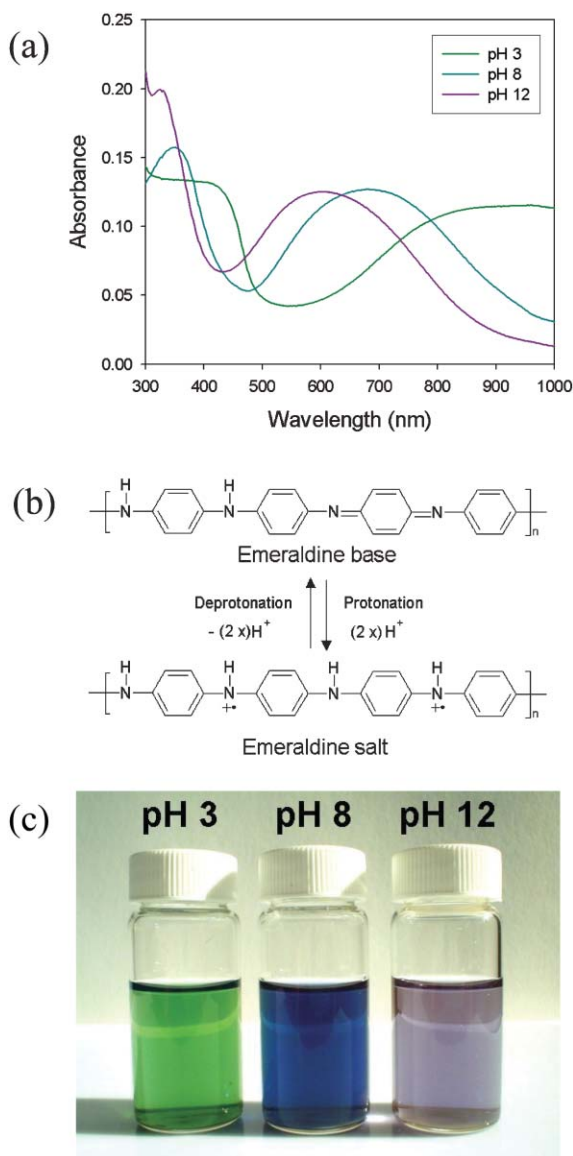
Fig. 4 a) UV-vis spectra of the silica–PANI core–shell nanoparticles for different pH values. b) Change of structure between emeraldine base and emeraldine salt during protonation and deprotonation. c) Photograph of the silica–PANI core–shell nanoparticles.

emeraldine base form of PANI. This result indicated that PANI was completely transformed from the emeraldine salt to the emeraldine base form by the deprotonation of PANI with increasing pH (Fig. 4b). The absorption at 310 nm is due to two different transitions of the π–π* transition and a transition from low-lying orbitals to the π_q orbital.

Fig. 4c is a photograph that shows the color change of the silica–PANI core–shell nanoparticles against the pH of the solution. At pH 3, the solution of the silica–PANI core–shell nanoparticles was in green. The color changed from green to blue and violet at increased pHs of 8 and 12, respectively. This result is consistent with the UV-vis spectral shift shown in Fig. 4a, indicating that PANI has been fully de-doped to the emeraldine base form. When PANI was re-doped by decreasing the pH of the

solution, a reversible color change from violet to green was observed. This pH-induced redox reversibility confirms the formation of the PANI shells in an electroactive form and suggests that the silica–PANI core–shell nanoparticles could be applied as a pH-responsive sensing material. The electrical conductivity of the silica–PANI core–shell nanoparticles with PANI in a doped state was measured in compressed pellet form by the four-probe method at room temperature and was found to be as high as 1.4 S cm^{-1}.

In summary, we have demonstrated the simple synthesis of silica–PANI core–shell nanoparticles by *in-situ* polymerization of positively charged anilinium ions adsorbed on the negatively charged silica surfaces. This simple process has allowed the formation of uniform PANI shells as thin as 2 nm on the silica cores, resulting in monodisperse core–shell nanoparticles. These silica–PANI core–shell nanoparticles also showed pH-responsive redox reversibility and relatively high electrical conductivity. This synthetic approach provides the formation of very thin layer shells with nanometer precision in thickness *via* electrostatic interactions, and might be expanded to fabricate various core–shell nano-structures composed of metallic, inorganic, or polymeric materials.

Notes and references

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