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Conductive Hollow Nanospheres of Polyaniline via Surface-Initiated Atom Transfer Radical Polymerization of 4-Vinylaniline and Oxidative Graft Copolymerization of Aniline

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1. Introduction

Hollow micro/nanospheres are potentially useful as encapsulants for drugs,[1−3] catalysts,[4] paints,[4] and enzymes,[3] as transducers for electronics,[5] and as absorption materials for sound.[5] To meet the demand for encapsulation, hollow spheres of carbon,[6,7] polymers,[8,9] metal,[10,11] and inorganic materials[1,12−14] have been prepared using polymeric or inorganic spherical particles as templates. The century-old polyaniline (PANI) has been of particular interest because of its good environmental stability,[16,17] controllable electrical conductivity,[18−20] and the ability to exist in a number of intrinsic redox states.[21,22] The unique physicochemical and solution-processable properties of the aniline polymers make them potentially useful for application in energy storage devices,[23] optoelectronic devices,[24] display devices,[25] electrodes and sensors,[26,27] corrosion protection of metals, and drug delivery.[28] Accordingly, the preparation of PANI hollow nanospheres should be of interest and importance. Excellent works on PANI hollow micro- and nanospheres, prepared from self-assembly and coating of PANI on emulsion, colloidal polystyrene, polyeletrolyte, and metal oxide templates, are available in the literature.[29−35]

Recent development in surface-initiated controlled/living polymerization has provided an alternative approach to the preparation of inorganic−organic core−shell hybrids with well-defined and controlled shell structures.[36−40] Nearly monodispersed hollow spheres with controllable shell thickness can be prepared from the removal of the core templates of these core−shell composites.[11,41,42] In this study, we report on a surface-initiated living radical polymerization approach to the preparation of well-defined PANI hollow nanospheres. The strategy is shown in Scheme 1. Initially, the atom transfer radical polymerization (ATRP) initiator, trichloro(4-chloromethylphenyl)silane, was immobilized on the surface of SiO_2 nanoparticles of about 25 nm diameter. Silica nanoparticles with surface-grafted polymer of 4-vinylaniline (SiO_2-*g*-PVAn) were prepared via surface-initiated ATRP of 4-vinylaniline (VAn). Subsequent surface oxidative graft copolymerization of aniline, using the aniline moieties of PVAn as the anchoring sites,[43] and removal of the silica cores by HF etching produced the well-defined P(VAn-*graft*-PANI) hollow nanospheres with a conductive shell of about 15−40 nm in thickness and core void of about 25 nm in diameter. The present approach allows the preparation of conductive PANI hollow nanospheres of controllable dimension (void dimension and shell thickness) and uniform size. Furthermore, the so-obtained hollow nanospheres are expected to have good structural integrity because of chain entanglements in the dense comb-shaped P(VAn-*g*-PANI) brushes which constitute the shell.

2. Results and Discussion

The atom transfer radical polymerization (ATRP) initiator, trichloro(4-chloromethylphenyl)silane, was immobilized on the silica nanoparticles of about 25 nm diameter through the reaction of the chlorosilyl group with the silanol group. The transmission electron microscopy (TEM) image of the initiator-immobilized silica nanoparticles (Figure 1a) shows that the surface-modified nanoparticles remain unagglomerated. The X-ray photoelectron spectroscopy (XPS) wide-scan spectrum (Figure 2a) and energy-dispersive X-ray (EDX) analysis results (Figure 3a) of the surface-modified nanoparticles indicate that the benzyl chloride initiators have been successfully immobilized on the silica surface. A chlorine content of about 1.44 wt % for the SiO_2-initiator nanospheres was obtained from elemental analysis. The corresponding surface benzyl chloride initiator concentration (ρ) of 2.4 initiators/nm^2 is comparable to the reported silane initiator density of 2.6 initiators/nm^2 for the silica particle surface.[37] Using the average cross-sectional area (A) of about 2 nm^2 for the vinyl and acrylate polymer brushes prepared via ATRP,[44] the surface initiator efficiency of the present system ($1/\rho A$) is estimated to be about 21%.

The silica-*graft*-poly(4-vinylaniline) (SiO_2-*g*-PVAn) nanospheres were prepared via surface-initiated ATRP of 4-vinylaniline (VAn) from the initiator-immobilized silica nanoparticles, using CuCl and *N*,*N*,*N′*,*N″*,*N″*-pentamethyldiethylenetriamine (PMDETA) as the catalyst system. The characteristics of the SiO_2-*g*-PVAn nanospheres prepared under different ATRP durations are summarized in Table 1. The chain length of PVAn brushes, and thus the thickness of the PVAn shell, on the silica nanospheres can be adjusted by changing the ATRP time. The number-average molecular weight (M_n) of PVAn, cleaved via HF etching, from the SiO_2-*g*-PVAn nanoparticles increases from 1.4×10^3 to 5.2×10^3 g/mol with the increase in polymerization time from 1.5 to 6 h, while the polydispersity index remains at around of 1.2 (Table 1). Table 1 also shows the theoretical M_n's of the PVAn brushes calculated from the initiator efficiency and density, the thickness of PVAn film, and the PVAn density of about 1 g/cm^3. They are comparable to those obtained from GPC measurements. Figure 2b shows the XPS wide-scan spectrum of the SiO_2-*g*-PVAn1 nanospheres described in Table 1. Prior to XPS analysis, the SiO_2-*g*-PVAn nanospheres were washed with copious amounts of THF, a good solvent for PVAn. The exhaustive washing procedures ensured the complete removal of PVAn homopolymer absorbed on the SiO_2-*g*-PVAn nanospheres. The appearance of strong C 1s and N 1s signals, as well as an N 1s spectrum with line shape and binding energy (399.4 eV) characteristic of those of the $-NH_2$ species[43] (inset of Figure 2b), suggests that PVAn has been successfully grafted on the silica nanospheres. The persistence of the Si 2s and Si 2p signals, albeit of substantially reduced intensities, in the XPS analysis is consistent with the presence of core−shell structured SiO_2-*g*-PVAn1 nanospheres having a PVAn shell thickness of about 3 nm,[45] which is less than the sampling depth of the XPS technique (∼7.5 nm in an organic matrix[46]).

Surface-initiated oxidative graft copolymerization of aniline from the SiO_2-*g*-PVAn nanospheres, using the aniline moieties

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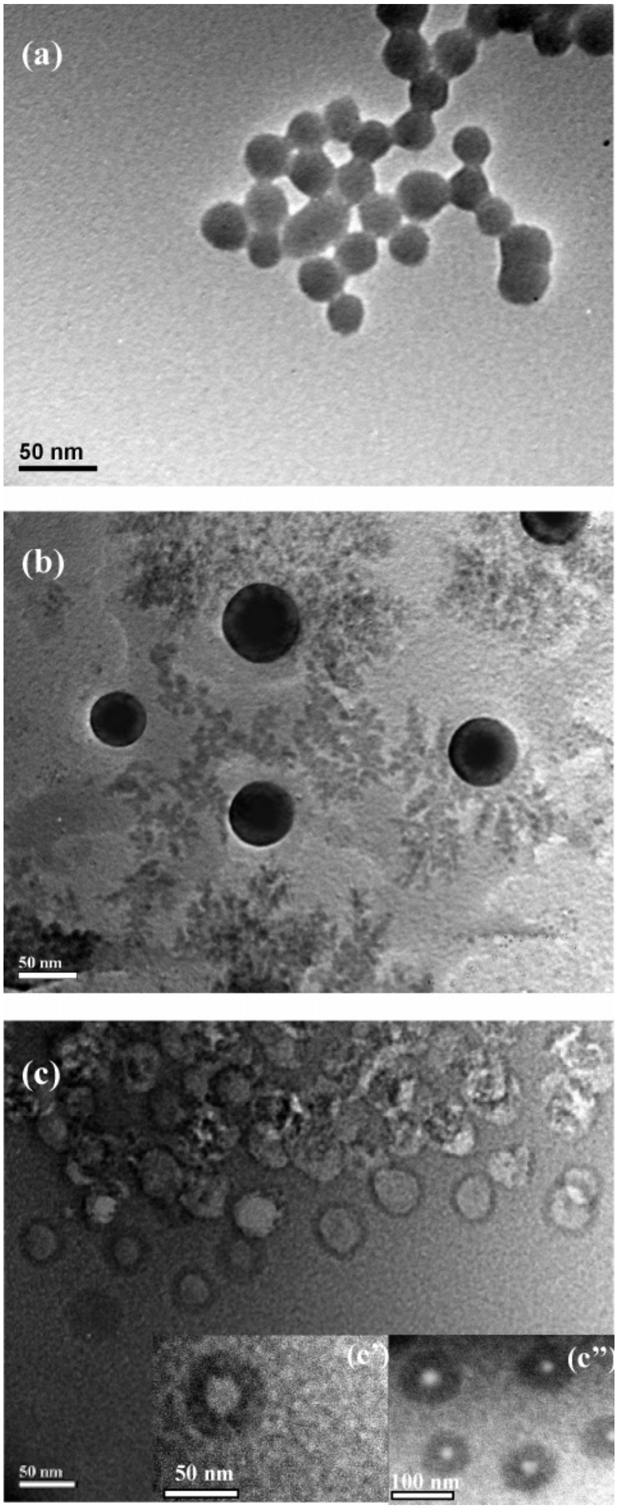


Figure 1. Transmission electron microscopy (TEM) images of (a) the trichloro(4-chloromethylphenyl)silane-immobilized silica nanoparticles and the silica-*graft*-poly(4-vinylaniline-*graft*-polyaniline) [SiO_2-*g*-P(VAn-*g*-PANI)1 nanospheres in Table 1, prepared from silica-*graft*-poly(4-vinylaniline) nanospheres, or SiO_2-*g*-PVAn1 nanospheres, of Table 1 via 0.5 h of oxidative graft copolymerization of aniline] (b) before and (c) after HF etching. Theinsets in (c) are the TEM images of hollow nanospheres with different shell thickness, derived from (c′) SiO_2-*g*-P(VAn-*g*PANI)2 nanospheres in Table 1 [prepared from SiO_2-*g*-PVAn1 nanospheres of Table 1 via 1.5 h of oxidative graft copolymerization of aniline] and (c″) SiO_2-*g*-P(VAn-*g*-PANI)3 nanospheres in Table 1 [prepared from SiO_2-*g*-PVAn1 nanospheres of Table 1 via 4 h of oxidative graft copolymerization of aniline].

of PVAn as the anchoring site,[43] produced the silica-*graft*-poly(4-vinylaniline-*g*-polyaniline), or SiO_2-*g*-P(VAn-*g*-PANI), core−shell nanospheres. The effect of grafted PVAn chain length on a solid substrate on the subsequent extent of oxidative graft copolymerization of aniline has been reported earlier.[47] Figure 1b shows the TEM image of the SiO_2-*g*-P(VAn-*g*-PANI)1 nanospheres of Table 1. Basically, a core−shell structure (dark-colored SiO_2 core and light-colored P(VAn-*g*-PANI) shell) was obtained. The disappearance of the Si signals in the XPS wide-scan spectrum of the SiO_2-*g*-P(VAn-*g*-PANI)1 nanospheres (Figure 2c) is consistent with the presence of a SiO_2-*g*-P(VAn-*g*-PANI) core−shell structure, with a shell thickness greater than the sampling depth of the XPS technique.[46] The presence of PANI chains in the shell of the SiO_2-*g*-P(VAn-*g*-PANI) nanosphere was also indicated by the marked increase in the C and N concentration, relative to the Si concentration, over those of the original SiO_2-*g*-PVAn nanospheres (compare the EDX spectra of Figure 3b,c). The atomic sensitivity of the Cu 2p signal is about 5 times that of the C 1s signal. Thus, any trace amount of Cu (down to 0.02 at. %) in the sample could still be detected by XPS.[48] The absence of Cu signals in the XPS and EDX analysis results of the SiO_2-*g*-PVAn and SiO_2-*g*-P(VAn-*g*-PANI) nanospheres indicates that the CuCl catalyst for ATRP has been completely removed during the process of precipitating SiO_2-*g*-PVAn nanospheres in methanol and subsequent oxidative graft copolymerization of aniline in an acid medium (see Experimental Section).

HF etching of the SiO_2-*g*-P(VAn-*g*-PANI) nanoparticles removed the SiO_2 cores and produced the HF-doped P(VAn-*g*-PANI) hollow nanospheres. The TEM image (Figure 1c) of the HF-etched SiO_2-*g*-P(VAn-*g*-PANI)1 nanospheres of Table 1 clearly reveals the hollow structure of nanospheres with a shell thickness of about 16 nm. Structural integrity of the shell or capsule is probably enhanced by the entangled PANI brushes as well as the cross-linked PANI chains from side reactions.[49] The almost disappearance of the Si signal and the predominance of carbon and nitrogen signals in the EDX spectrum of the hollow nanospheres in Figure 3d are consistent with the successful removal of the silica cores and the formation of P(VAn-*g*-PANI) hollow nanospheres. The persistence of a trace amount of Si in the P(VAn-*g*-PANI) hollow nanospheres (Figure 3d) after HF treatment suggests that the Si−O−Si bridges between the trifunctional initiation sites remain intact to provide a link for the end-attached chains. P(VAn-*g*-PANI) hollow nanospheres of different shell thicknesses are shown in the insets of Figure 1c, and their characteristics are also summarized in Table 1. With the increase in oxidative graft copolymerization time of aniline from 0.5 to 4 h, the shell thickness of the hollow nanospheres has increased correspondingly from 16 to 41 nm. For the hollow nanosheres with a thin P(VAn-*g*-PANI) shell (Figure 1c), a slight expansion of the hollow core has occurred after the HF etching of the SiO_2 core. Nevertheless, the thin shell consisting of dense comb-shaped P(VAn-*g*-PANI) chains with entangled or cross-linked[49] PANI brushes remained intact. The self-assembled and HF protonated P(VAn-*g*-PANI) hollow nanospheres exhibit conductivity in the range of $10^{-2}-10^{-1}$ S cm^{-1} (Table 1), or about 1−2 orders of magnitude lower than that of the protonated aniline homopolymer.[19] The apparently lower conductivity for the self-assembled hollow nanospheres can be attributed to the presence of core voids and interstitial spaces in the layer. The conductivity of the self-assembled PANI hollow nanospheres is also lower than that of the PANI pellets from compressed PANI hollow nanospheres.

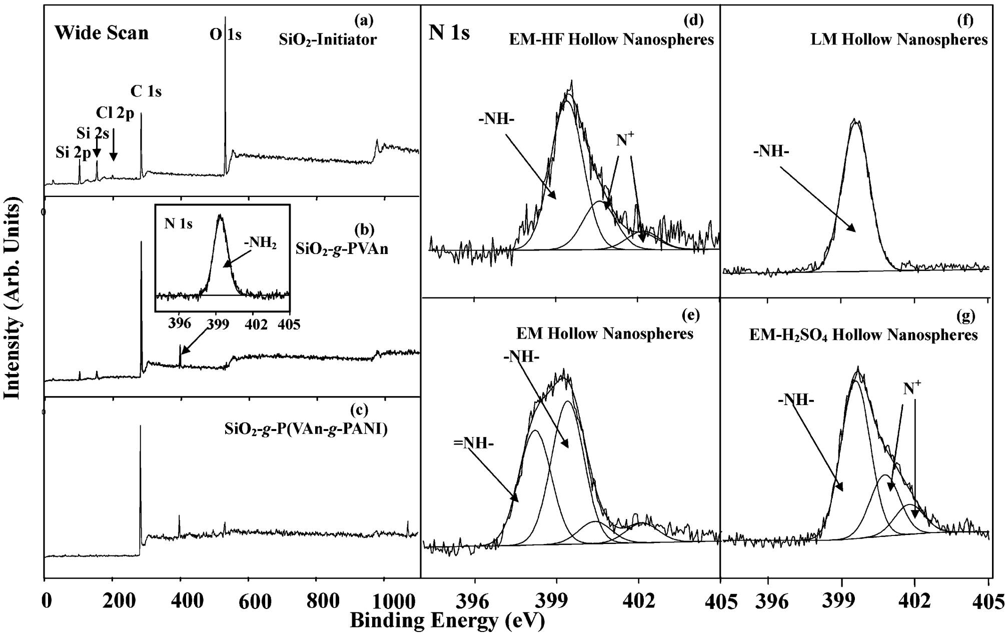
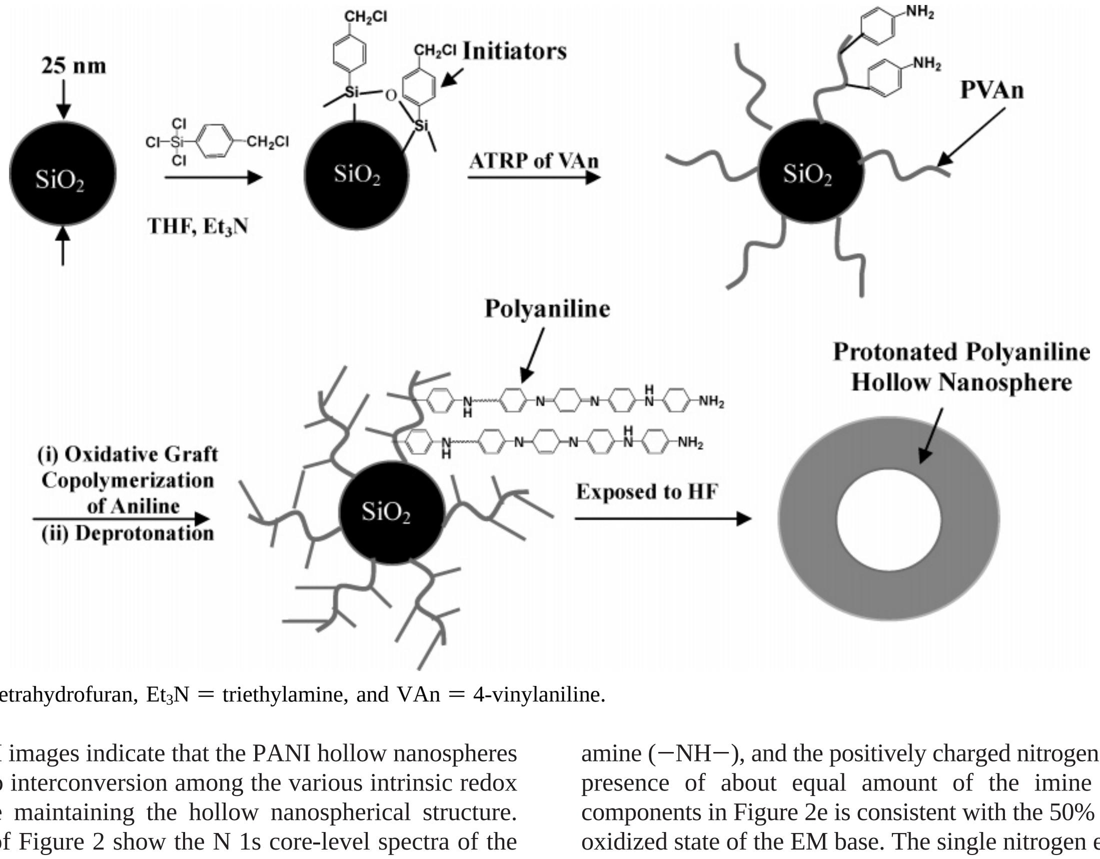


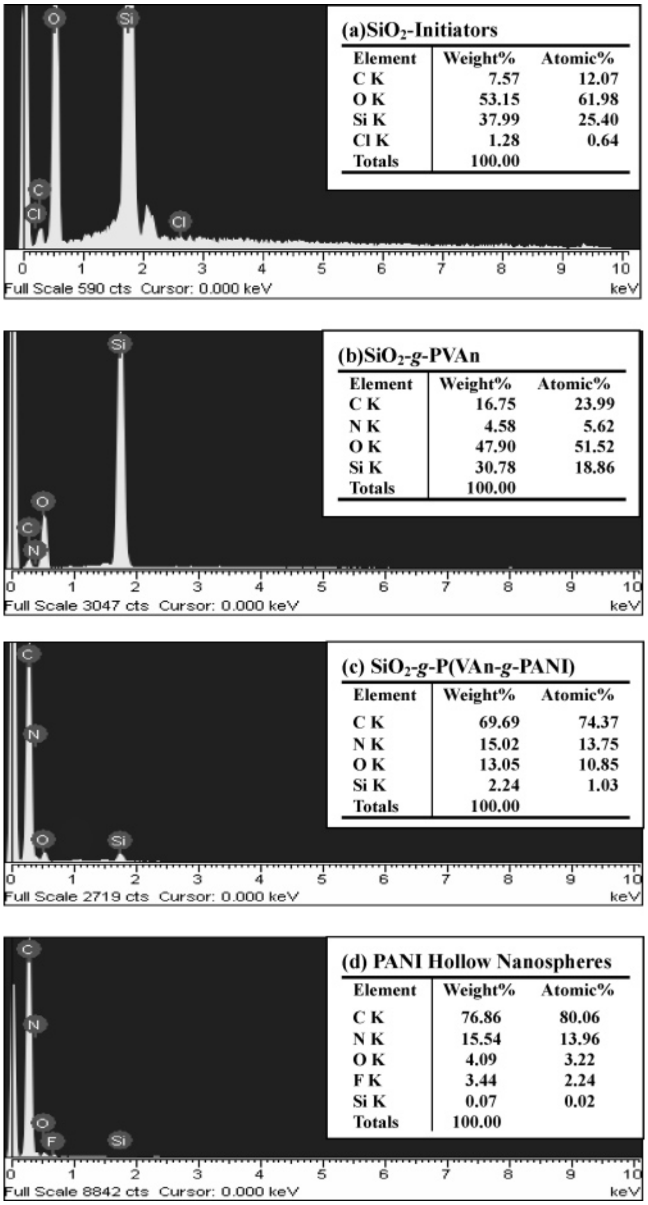
Figure 2. X-ray photoelectron spectroscopy (XPS) wide-scan spectra of the (a) trichloro(4-chloromethylphenyl)silane-immobilized silica nanospheres, (b) silica-*graft*-poly(4-vinylaniline) nanospheres [SiO_2-*g*-PVAn1 nanospheres in Table 1 from 1.5 h of surface-initiated atom transfer radical polymerization of 4-vinylaniline], and (c) silica-*graft*-poly(4-vinylaniline-*graft*-polyaniline) nanospheres [SiO_2-*g*-P(VAn-*g*-PANI)1 nanospheres in Table 1 from 0.5 h of oxidative graft copolymerization of aniline with the SiO_2-*g*-PVAn1 nanosphere surface]. XPS N 1s core-level spectra of the P(VAn-*g*-PANI) hollow nanospheres [from HF etching of the SiO_2-*g*-P(VAn-*g*-PANI)1 nanospheres in Table 1] in their (d) HF-protonated (as-prepared) form, (e) EM base form, (f) LM base form, and (g) 1 M H_2SO_4 reprotonated EM form.

Scheme 1. Preparation of Conductive Poly(4-vinylaniline-*graft*-polyaniline), or P(VAn-*g*-PANI), Hollow Nanospheres via Surface-Initiated Atom Transfer Radical Polymerization (ATRP) and Oxidative Graft Copolymerization[a]



[a] THF = tetrahydrofuran, Et_3N = triethylamine, and VAn = 4-vinylaniline.

The TEM images indicate that the PANI hollow nanospheres can undergo interconversion among the various intrinsic redox states while maintaining the hollow nanospherical structure. Parts d−g of Figure 2 show the N 1s core-level spectra of the PANI hollow nanospheres (from SiO_2-*g*-P(VAn-*g*-PANI)1 of Table 1) in their HF-protonated (as prepared) form, neutral EM base form, fully reduced leucoemeraldine (LM) base form, and the H_2SO_4-reprotonated EM base (EM-H_2SO_4) form, respectively. The peak components at BEs of about 398.2, 399.4, and >400 eV correspond to the quinonoid imine (=N−), benzenoid amine (−NH−), and the positively charged nitrogen (N^+).[21] The presence of about equal amount of the imine and amine components in Figure 2e is consistent with the 50% intrinsically oxidized state of the EM base. The single nitrogen environment at the BE of about 399.4 in Figure 2f indicates that the PANI hollow nanosperes have been converted to the fully reduced LM state. Reprotonation of the EM base by H_2SO_4 has resulted in the disappearance of the =N− species and the appearance of a corresponding amount of the N^+ species (Figure 2g), as protonation occurred preferentially at the imine nitrogen.[19−21]



(a)SiO_2-Initiators

Element	Weight%	Atomic%
C K	7.57	12.07
O K	53.15	61.98
Si K	37.99	25.40
Cl K	1.28	0.64
Totals	100.00	

(b)SiO_2-*g*-PVAn

Element	Weight%	Atomic%
C K	16.75	23.99
N K	4.58	5.62
O K	47.90	51.52
Si K	30.78	18.86
Totals	100.00	

(c) SiO_2-*g*-P(VAn-*g*-PANI)

Element	Weight%	Atomic%
C K	69.69	74.37
N K	15.02	13.75
O K	13.05	10.85
Si K	2.24	1.03
Totals	100.00	

(d) PANI Hollow Nanospheres

Element	Weight%	Atomic%
C K	76.86	80.06
N K	15.54	13.96
O K	4.09	3.22
F K	3.44	2.24
Si K	0.07	0.02
Totals	100.00	

Figure 3. Energy-dispersive X-ray (EDX) analysis spectra of (a) the trichloro(4-chloromethylphenyl)silane-immobilized silica nanoparticles, (b) the silica-*graft*-poly(4-vinylaniline) nanospheres [SiO_2-*g*-PVAn1 nanospheres in Table 1 from 1.5 h of surface-initiated atom transfer radical polymerization of 4-vinylaniline], and the silica-*graft*-poly(4-vinylaniline-*graft*-polyaniline) nanospheres [SiO_2-*g*-P(VAn-*g*-PANI)1 nanospheres in Table 1 from 0.5 h of oxidative graft copolymerization of aniline with the SiO_2-*g*-PVAn1 nanosphere surface] (c) before and (d) after HF treatment. Insets c′ and c″ show the TEM images of the hollow nanospheres obtained from HF etching of the respective SiO_2-*g*-P(VAn-*g*-PANI)2 nanospheres [from 1.5 h of oxidative graft copolymerization of aniline with the SiO_2-*g*-PVAn1 nanosphere surface] and SiO_2-*g*-P(VAn-*g*-PANI)3 nanospheres [from 4 h of oxidative graft copolymerization of aniline with the SiO_2-*g*-PVAn1 nanosphere surface] of Table 1.

3. Conclusions

In summary, a controlled polymerization approach to the preparation of polyaniline (PANI) hollow nanospheres was described. Surface-initiated atom transfer radical polymerization (ATRP) of 4-vinylaniline (VAn) from the initiator-immobilized SiO_2 nanoparticles and subsequent oxidative graft copolymerization of aniline allowed the preparation of well-defined SiO_2-*g*-P(VAn-*g*-PANI) core−shell structures. Conductive P(VAn-*g*-PANI) hollow nanospheres with different shell thickness could be readily prepared by varying the ATRP and the oxidative graft copolymerization time. Obviously, the dimension of the hollow cores could be further controlled by changing the size of the initiator-immobilized silica nanoparticles. The resulting PANI hollow nanospheres exhibited intrinsic redox states and deprotonation/reprotonation behavior characteristic of those of the aniline homopolymer.

4. Experimental Section

Initiator Immobilization on Silica Nanoparticles. Dried SiO_2 nanoparticles (2.0 g) of about 25 nm diameter, 3.0 g (9.5 mmol) of trichloro(4-chloromethylphenyl)silane (97%), and 20 mL of absolutely dried THF were introduced into a two-necked flask. Triethylamine (1.2 mL, 8.6 mmol) in THF (5.0 mL) was added dropwise, with stirring, under an argon atmosphere. The reaction mixture was left to stand for 8 h and then exposed to air for another 18 h. After five cycles of ethanol and THF rinsing, and separation by centrifugation, about 1.8 g of white initiator-immobilized SiO_2 nanoparticles was obtained. The chlorine concentration was about 1.44 wt %, as determined from elemental analysis. This chlorine concentration corresponded to about 2.4 benzyl chloride initiators per nm^2 of the particle surface.[44]

Surface-Initiated Atom Transfer Radical Polymerization (ATRP) of 4-Vinylaniline. About 0.1 g of the initiator-immobilized silica nanoparticles, 1.2 mL (9 mmol) of 4-vinylaniline (VAn, 90%), 1 mL of dry THF, and 4 mg (0.04 mmol) of CuCl (99.7%) were introduced into a dry Pyrex test tube. After purging with argon for 20 min, about 0.04 mmol of *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA, 99%) was added, and the reaction tube was sealed with a rubber stopper. Thus, the molar ratio of [4-vinylanilne]:[initiator]:[CuCl]:[PMDETA] was about 225:1:1:1. Surface-initiated ATRP was carried out under continuous stirring at 110 °C. The reaction time was varied from 1.5 to 6 h. At the end of each reaction, the reaction mixture was diluted with 5 mL of THF, and the product was precipitated into 100 mL of methanol. The product was redispersed into 10 mL of THF and centrifuged to remove the physically adsorbed 4-vinylaniline homopolymer. The process was repeated another two times.

Oxidative Graft Copolymerization of Aniline. About 0.1 g of the 4-vinylaniline polymer (PVAn) grafted SiO_2 nanospheres, or SiO_2-*g*-PVAn nanospheres, and 1 mL (0.01 mol) of aniline were introduced slowly into 30 mL of 1.0 M HCl under magnetic stirring. About 0.6 g (2.6 mol) of $(NH_4)_2S_2O_8$ was dissolved in 20 mL of 1.0 M HCl. The oxidant solution was introduced into the SiO_2-*g*-PVAn and aniline reaction mixture at 0 °C. The oxidative graft copolymerization was carried out for 0.5−4 h. The aniline moiety of the VAn units served as the anchoring and initiation sites for the oxidative graft copolymerization of aniline.[43] The polyaniline (PANI) in the shell was then converted to the neutral emeraldine (EM) base by treatment with excess 0.5 M NaOH. The product was redispersed into 1-methyl-2-pyrrolidone (NMP, a good solvent for EM base[21]), and centrifuged to remove the adsorbed PANI homopolymer in its EM base form. The process was repeated several times until no PANI homopolymer was found in the NMP solutions. The SiO_2 cores were removed by immersing the SiO_2-*g*-P(VAn-*g*-PANI) nanospheres into 10% HF for 24 h. Interconversions among the various intrinsic redox and protonation states of the PANI hollow nanospheres were carried out as previous described.[19−22] Thus, the protonated PANI was converted to the EM base by treatment with 0.5 M NaOH, the EM base to the fully reduced leucoemeraldine (LM) base by treatment with phenylhydrazine, and the EM base to the reprotonated PANI by treatment with 1 M H_2SO_4.

Characterization. Gel permeation chromatography (GPC) was performed on an HP 1100 high-pressure liquid chromatography (HPLC), equipped with a HP 1047A refractive index detector and a PLgel MIXED-C 300 × 7.5 mm column (packed with 5 μm particles of different pore size). The column packing allowed the separation of polymers over a wide molecular weight range of 200−3 000 000. THF was used as the eluent at a flow rate of 1 mL/min at 35 °C. Polystyrene standards were used as the references. XPS

Table 1. Characteristics of the Conductive Polyaniline Hollow Nanospheres

sample	polymerization time (h)	mol wt[a] (g/mol)	PDI[a]	mol wt[d] (g/mol)	particle size[e] (nm)	shell thickness[e] (nm)	shell thickness[f] (nm)	conductivity	
								σ_1[g] (S/cm)	σ_2[h] (S/cm)
SiO_2-*g*-PVAn1[b]	1.5	1.4×10^3	1.16	2.0×10^3		3			
SiO_2-*g*-PVAn2[b]	3.0	2.5×10^3	1.23	3.9×10^3		5			
SiO_2-*g*-PVAn3[b]	6.0	5.2×10^3	1.18	7.5×10^3		9			
SiO_2-*g*-P(VAn-*g*-PANI)1[c]	0.5				61	14	16	2×10^{-2}	8×10^{-2}
SiO_2-*g*-P(VAn-*g*-PANI)2[c]	1.5				83	24	26	3×10^{-2}	2×10^{-1}
SiO_2-*g*-P(VAn-*g*-PANI)3[c]	4.0				111	44	41	1×10^{-1}	3×10^{-1}

[a] Number-average molecular weight of poly(4-vinylaniline), or PVAn, obtained from HF etching of the corresponding nanospheres. PDI = polydispersity index (weight-average molecular weight/number-average molecular weight or M_w/M_n). [b] Silica-*graft*-poly(4-vinylaniline) nanospheres prepared from the initiator-immobilized silica nanospheres at a molar feed ratio of [4-vinylaniline]:[initiator]:[CuCl]:[PMDETA] = 225:1:1:1. The amount of initiator on the SiO_2 surface was determined by element analysis. PMDETA = *N,N,N′,N″,N″*-pentamethyldiethylenetriamine; initiator = trichloro(4-chloromethylphenyl)silane. [c] Silica-*graft*-poly(4-vinylaniline-*graft*-polyaniline) nanospheres obtained from the SiO_2-*g*-PVAn1 nanospheres via oxidative graft copolymerization of aniline. [d] Theoretical values calculated from the initiator efficiency and density and film thickness of surface-initiated ATRP of 4-vinylaniline. [e] Average shell thickness and particle size of SiO_2-*g*-P(VAn-g-PANI) determined from transmission electron microscope (TEM) image before HF treatment. The shell thickness of SiO_2-*g*-PVAn was estimated simulation. [f] Average shell thickness determined from TEM image after HF treatment. [g] Conductivity of self-assembled, HF-protonated hollow nanospheres. [h] Conductivity of compressed/compacted nanospheres in pellet form.

measurements were carried out on a Kratos AXIS HSi spectrometer, equipped with a monochromatized Al Kα X-ray source (1486.6 eV photons). A JEOL 2010 TEM was used to characterize the morphology of nanoparticles. Energy dispersive X-ray (EDX) analysis was carried out on a JEOL JSM5600LV SEM. Conductivity of compressed pellets and self-assembled layers of the PANI hollow nanospheres were measured by the four-probe method using a digital multimeter (Keithley, model 2001) and a programmable dc voltage/current generator (HP, model 6212B) as the current source. The self-assembled layers of the PANI hollow nanospheres were prepared by spin-coating of an aqueous acid dispersion of PANI hollow nanospheres on a clean Si(100) wafer.

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