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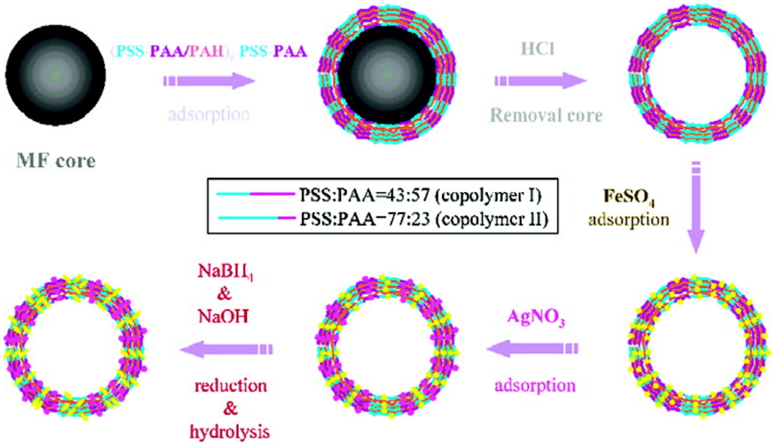

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Synthesis of Two Types of Nanoparticles in Polyelectrolyte Capsule Nanoreactors and Their Dual Functionality

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Abstract: Polyelectrolyte multilayer capsule reactors (PEMCRs) for the synthesis of two types of nanoparticles were prepared. The tunable PEMCRs containing two different functional groups that can be used to synthesize two types of nanoparticles simultaneously and to control the composition of two types of nanoparticles within the shell of PEMCs. These PEMCRs enabled the composition as well as the amount of the loaded two types of nanoparticles within the shell of PEMCs to be controlled by the copolymer ratio and the number of reaction cycles. Another interesting finding is that, as a result of the synthesis of two types of nanoparticles, these specially designed PEMCs containing both silver and goethite nanocrystals can be used as antimicrobial capsules, which can move by an external magnetic field. Such a technology has the potential for use in sterilization at the desirable sites.

Introduction

Polyelectrolyte multilayer (PEM) systems have recently emerged as useful tools for the synthesis of novel organics[1−3] and inorganics.[4−7] Submicro or nanoreactors consisting of PEMs are particularly widely used in the synthesis of metal,[8−12] semiconductor,[13,14] and metal oxide/hydroxide[15−17] nanoparticles because polyelectrolyte multilayer reactors (PEMRs) for nanomaterial synthesis have the following advantages: (i) absence of particle aggregates, (ii) synthesis occurs exclusively within the reactor, (iii) fabrication of unique inorganic/inorganic and inorganic/organic hybrid structures, and (iv) synthesis of novel nanomaterials that are impossible or difficult to synthesize using conventional techniques.[18] Nanoparticle synthesis within PEMRs can be carried out by loading precursors into PEMs, followed by a chemical or physical treatment. PEMRs can be produced in an assortment of geometries. One is polyelectrolyte multilayer films (PEMFs) that can be fabricated on planar substrates by the stepwise adsorption of oppositely charged polyelectrolytes.[19] PEMFs provide reaction sites for the synthesis of metallic and semiconducting nanoparticles from the reduction or hydrolysis of the corresponding metal ions, which are selectively bound to functional groups within the PEMFs. The concentration and size of synthesized metallic/semiconducting nanoparticles within PEMFs can be tuned by adjustment of the concentration of reactants and the number of ion-exchange/reaction cycles used.[8,10,12−14] The other is polyelectrolyte multilayer capsules (PEMCs) that can be also prepared by the layer-by-layer (LbL) deposition of polyelectrolytes onto 3D structural templates, followed by template dissolution.[20,21] In the case of PEMCs, the interior of the capsules is used as reaction sites, which provide a confined space in which organic or inorganic materials with unique properties can be produced. In a previous study, we demonstrated that immobilized polymers produced in PEMCs as a confined space have a much higher molecular weight than polymers produced in bulk solution as a result of both immobilization and confined-space effects.[3] The shell of a PEMC can also be used as a reaction site. In addition, PEMCs have the advantage that they can move by means of external forces.[22,23]

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It is known that ethyleneimine, carboxylic acid, amine, and sulfonate groups within PEMs can be used as binding sites for the adsorption of metal ions for nanoparticle synthesis.[12−14,24−26] The number of incorporated functional groups into PEMs determines the number of types of the ultimately synthesized nanoparticles. However, each functional group has been used to synthesize only one type of metallic or semiconducting nanoparticle within the PEMs.[8−14] With monofunctional group-containing PEMRs, it has been difficult to produce various nanoparticles simultaneously and to tune their composition within PEMs due to the limited incorporation of necessary functional groups into PEMs.

Herein we report on tunable polyelectrolyte multilayer capsule reactors (PEMCRs) containing two different functional groups that can be used to synthesize two types of nanoparticles simultaneously and to control the composition of two types of nanoparticles within the shell of PEMCs. To the best of our knowledge, the in situ synthesis of two types of nanoparticles in the shell of PEMCRs, which have tunable two different functional groups, has not yet been reported. To incorporate two different functional groups into PEMCRs, copolymerized polyelectrolytes composed of poly(styrene sulfonate) (PSS) and poly(acylic acid) (PAA) were prepared as a function of molar ratio and used with poly(allylamine hydrochloride) (PAH) to fabricate PEMCRs. After the formation of PEMCRs, metal ions were loaded from an aqueous solution into the PEMCRs and were then reacted to create two types of nanoparticles within the PEMCRs. We demonstrate that novel PEMCRs composed of PSS−PAA/PAH can be used not only to produce two types of nanoparticles simultaneously but also to tune their compositions within PEMCs. In addition, position controllable goethite/silver nanoparticle-embedded polyelectrolyte capsules, which are able to move by applying an external magnetic field, were explored. Such a technology has the potential for use in sterilization at the desirable sites.

Experimental Section

Materials. Styrene sulfonate (SS), acrylic acid (AA), poly(allylamine hydrochloride), PAH (M_w 15 000), silver nitrate ($AgNO_3$), iron(II) sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$), sodium borohydride ($NaBH_4$), and sodium hydroxide were purchased from Aldrich. Weakly cross-linked MF particles were purchased from Microparticle (GmbH). *Escherichia coli* (KCCM 41036) was purchased from the Korean Culture Center of Microorganisms (KCCM). All commercial materials were used without further purification. The water used in all experiments was prepared in a three-stage Milli-Q plus 185 purification system and had a resistivity higher than 18 MΩ cm.

Copolymer Synthesis. To incorporate two different functional groups into a polyelectrolyte, copolymers I and II were copolymerized using different SS/AA ratios. A solution containing styrene sulfonate [SS, 0.15 g (I), 0.3 g (II)], acrylic acid [AA, 0.053 mL (I), 0.053 mL (II)], potassium peroxodisulfate [KPS, 2 mg (I), 3.5 mg (II)], *N*,*N*,*N*,*N*-tetramethylethylenediamine (0.02 mL), and DI water (4 mL) was purged with nitrogen for 5 min and then sealed in a capped tube. The sealed tube was then heated at 40 °C for 3 h. After the polymerization, the product was purified by dialysis (Spectra/pro-membrane, MWCO: 15000) twice. Polymers were dried overnight by freeze-dry. The contents of the SS/AA units in the copolymers I and II, as determined from the ^1H NMR spectra, were 43−57 (I) and 77−23 (II) mol %, respectively.

PEMCR Preparation. Detailed procedures for the formation of PEMCRs were as follows: 1.5 mL of PSS−PAA solution (2 mg/mL) was added to 0.12 mL of an aqueous suspension of positively charged MF particles (10 wt %) with a diameter of 1.87 μm. The dispersion was vigorously agitated on a shaking apparatus for 15 min to allow the polyelectrolytes to adsorb to the MF particles. The dispersion was centrifuged at 10 000*g* for 3 min, the supernatant removed, and 1.5 mL of water was added. The particles were then redispersed by gentle shaking. The centrifugation/wash/dispersion cycle was repeated three times to ensure the removal of free polyelectrolytes from solution. After the formation of PSS−PAA layer outside MF cores, PAH (1.5 mL of 1 mg/mL) layers were deposited using an LbL assembly technique. The adsorption and rinsing steps were repeated until the desired number of layers was obtained. After the deposition of 17 layers of polyelectrolytes, the template MF core was removed with 0.15 M HCl (pH < 1), and consequently, PEMCRs were obtained.

Synthesis of Two Types of Nanoparticles within the PEMCR. Details of the in situ synthesis of two types of nanoparticles within the PEMCRs are as follows: 1.5 mL of an $FeSO_4$ solution (0.04 g/mL) was added to 0.12 mL (0.15 wt %) of an aqueous suspension of PEMCRs. The dispersion was vigorously agitated on a shaking apparatus for 12 h to allow iron ions to adsorb to the sulfonate, amine, and carboxylate groups of the polyelectrolytes. The dispersion was centrifuged at 10 000*g* for 3 min, the supernatant removed, and 1.5 mL of water added. This rinsing step was repeated three times; 1.5 mL of a $AgNO_3$ solution (0.028 g/mL) was added to an aqueous suspension of the resulting capsules. The dispersion was vigorously agitated on a shaking apparatus for 12 h, where the iron ions attached to carboxylate groups of PAA were replaced by silver cations. The rinsing step was the same as described above. The Fe(II)- and Ag(I)-containing PEMCRs were first reduced in 1 mM $NaBH_4$ solution for 30 min and then hydrolyzed in a 0.6 mM NaOH solution for 30 min. A rinsing step was performed between the reduction and hydrolysis reactions. Reaction cycles were repeated until the desired number of reaction cycles had been achieved.

Antimicrobial Test. *Escherichia coli* was grown for a 12 h incubation at 37 °C by suspending a colony-forming unit in 5 mL of Luria-Bertani (LB) broth. This culture was taken from the incubator and washed (sterilized DI water) prior to spectroscopy measurements. Optical density spectra were recorded by the addition of a goethite/silver-embedded capsule suspension (0.03 mL, 0.23 wt %) or goethite-embedded capsule suspension into the *Escherichia coli* suspension (1.5 mL).

Characterization. ζ-Potentials of particles dispersed in water were measured on a OTSUKA (ELS 8000) instrument. UV−vis spectra of cell suspensions were recorded using a Varian spectrometer (Cary 1E). FE-SEM micrographs were obtained using a Hitachi (S-4700) microscope. For FE-SEM/EDX analysis, a drop of sample solution was applied to a silicon wafer and dried at room temperature overnight. FE-SEM measurements after platinum coating of the sample were performed. The elemental mapping analyses were carried out for 200 s using an energy-dispersive X-ray spectrometer equipped from SEM at 15 kV. FE-TEM measurements were performed on a Philips (TECNAI F20) microscope operating at 200 kV. Samples were prepared by applying a drop of the sample solution to a carbon-coated copper grid. The X-ray diffraction (XRD) pattern was obtained using a Rigaku X-ray diffractometer equipped with a Cu Kα source.

Results and Discussion

Figure 1 shows the fabrication of specially designed PEMCRs and the synthesis of two types of nanoparticles within the shell of PEMCRs. PSS−PAA and PAH were used as the negative

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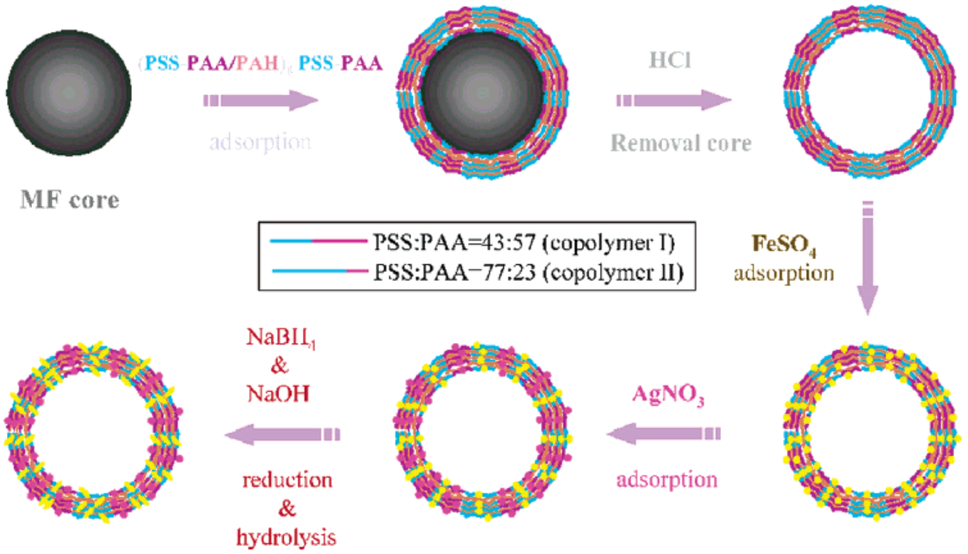

Figure 1. Schematic illustration of the procedures used in the fabrication of PEMCRs via the layer-by-layer assembly method using PSS−PAA/PAH and the synthesis of two types of nanoparticles within the shell of PEMCRs in the Fe−Ag reaction sequence.

and positive polyelectrolytes, respectively. Two types of PSS−PAAs with different molar ratios were copolymerized. The relative PSS and PAA compositions (mol %) within the copolymers were determined by ^{1}H NMR spectroscopy (as shown in inset of Figure 1). PEMCRs were fabricated by the stepwise adsorption of oppositely charged polyelectrolytes onto sacrificial melamine−formaldehyde (MF) colloidal particles, followed by decomposition of the cores at a low pH (pH < 1). $FeSO_4$ and $AgNO_3$ were added to dispersions of PEMCRs for nanoreactor chemistry of nanoparticles. Sulfonate, carboxylate, and amine groups of polyelectrolytes were mainly utilized to adsorb Fe^{2+} metal ions. Fe^{2+} metal ions attached to carboxylate groups of PAA were displaced by addition of Ag^+ metal ions. Figure SI1 in the Supporting Information shows that Fe^{2+} within the PSS/PAH multilayers is hard to replace with Ag^+, while Fe^{2+} within the PAA/PAH multilayers could be replaced by Ag^+ to some extent. These results indicate that the composition of two types of nanoparticles within the PSS−PAA/PAH multilayers can be controlled by copolymer ratio in Fe−Ag reaction sequence. Finally, treatment with $NaBH_4$ and NaOH was followed for the synthesis of silver nanoparticles and goethite nanocrystals, respectively. Goethite nanocrystals are formed according to the following reactions.[27]

$$FeSO_4 + 2\,NaOH \rightarrow Fe(OH)_2 + Na_2SO_4$$

$$4Fe(OH)_2 + O_2 \rightarrow 4\,FeOOH + 2H_2$$

The formation of PEMs on MF particles was monitored by ζ-potential measurement. Figure 2 represents the ζ-potential recorded after alternative adsorption of polyelectrolytes for the MF/[(PSS−PAA)/PAH]$_8$PSS−PAA system. The ζ-potential alternates between positive and negative values, indicating the successful recharging of particles coated with polyelectrolytes. The ζ-potential data suggested that multilayer formation of PSS−PAA/PAH was successfully carried out on the MF template particles.

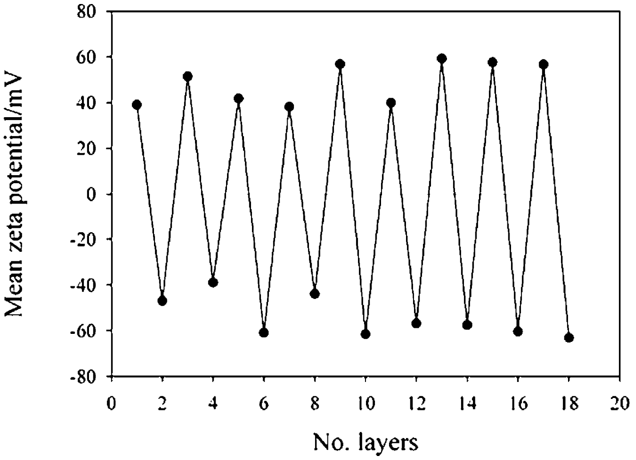

Figure 2. ζ-Potential of PSS−PAA/PAH-coated particles as a function of the number of layers deposited. Even and odd numbers represent the deposition of PSS−PAA and PAH (except 1 (MF)), respectively. PSS−PAA layer was initially deposited on the MF template. Experiments were repeated three times, and the average value was used.

Figure 3 shows FE-SEM micrographs of PEMCRs after the synthesis of two types of nanoparticles using two PSS−PAA copolymers with different compositions and different reaction cycles. Copolymer II has a higher PSS ratio (77 mol %) than that of copolymer I (43 mol %). PEMCRs from both copolymers I and II were covered with goethite nanocrystals in the form of a needlelike structure (Figure 3 and insets). Silver nanoparticles were difficult to observe in SEM micrographs because the size of silver particles was much smaller than goethite nanocrystals and the capsule surface was thickly covered with goethite nanocrystals. The presence of silver nanoparticles is described in detail in the TEM analysis.

The concentration and size of goethite nanocrystals within the shell layers were increased when the reaction was repeated three times (Figure 3b,d and insets). The surface morphology of copolymer II-based PEMCRs after synthesis of two types of nanoparticles also showed the same phenomena. However, the concentration of goethite nanocrystals within the shell layers was higher than that of copolymer I-based PEMCRs because copolymer II contains more PSS units that are capable of

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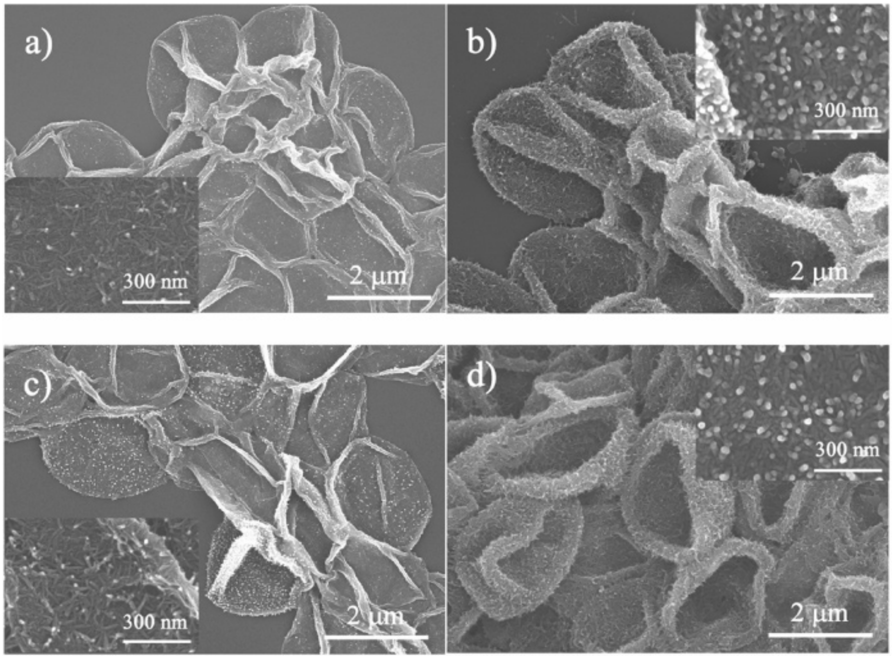


Figure 3. FE-SEM micrographs of two types of nanoparticles within the shell of PEMCRs made from (a,b) copolymer I (PSS−PAA ratio, 43−57) and (c,d) copolymer II (PSS−PAA ratio, 77−23), and after the different number of reaction cycles (a,c) one time, (b,d) three times. Average particle sizes of goethite nanocrystals are (a) 11 nm in width and 63 nm in length, (b) 18 and 74 nm, (c) 14 and 68 nm, (d) 20 and 79 nm. The average particle sizes of goethite were measured from SEM and TEM images. (Approximately 50 nanoparticles were measured to calculate the average size.) The insets show higher magnification images of the capsule surface.

goethite synthesis (Figure 3c and inset). The average particle sizes of the goethite nanocrystals were slightly increased from copolymer I-based PEMCRs (Figure 3a) to copolymer II-based ones (Figure 3c). Therefore, when $FeSO_4$ was hydrolyzed, an increase in the number of reaction cycles influenced both particle sizes and concentration, whereas increasing the PSS content within the copolymer mainly influenced particle concentration.

After the synthesis of two types of nanoparticles, the PEMCs showed a thicker shell as a function of reaction cycles than that of the original capsules due to the two types of nanoparticles grown within the shell layer. The size of the two types of nanoparticle-embedded capsules does not exceed the original size of the capsules. The resulting capsules have a different and complicated surface morphology due to the formation of two types of nanoparticles. In the case of goethite nanocrystals with a small concentration, the crystals showed a needlelike structure grown parallel to the shell (inset in Figure 3a), whereas the others showed a perpendicular needlelike structure (inset in Figure 3d). It seems that goethite nanocrystals after initial growth parallel to the shell begin to grow in a perpendicular direction to the shell as the amount of nanocrystals increased. SEM micrographs clearly reveal that the concentration, size, and other morphology of goethite nanocrystals grown within the PEMCRs can be tuned by adjusting the copolymer ratio and the number of reaction cycles.

TEM measurements were performed to investigate the inner structure of two types of nanoparticle-embedded capsules. TEM micrographs of copolymers I- and II-based PEMCRs after synthesis of two types of nanoparticles show that both silver nanoparticles and goethite nanocrystals were successfully synthesized within the shell, with a spherical shape and a needlelike structure, respectively (cf. Figure 4). As shown the inset of Figure 4c, higher magnification TEM reveals that different crystal structures of the two types of nanoparticles are clearly present in the shell of PEMCRs. In the case of goethite nanocrystals that have overgrown within the shell, the “shadowing” feature, which indicates a more electron-dense region, was observed (Figure 4e). The amount of goethite nanocrystals grown within the PEMCRs can be controlled by the number of reaction cycles (as shown in a and b, or d and e in Figure 4) and the copolymer ratio of PSS−PAA (a−d or b−e in Figure 4). Similar to the results from SEM analysis, repeated reaction cycles increased the amount of the particles synthesized as clearly recognized from the comparison of a and b (also d and e) in Figure 4. Copolymer II-based PEMCRs (d,e in Figure 4) represented more goethite nanocrystals and less silver nanoparticles than copolymer I-based PEMCRs (a,b in Figure 4) because copolymer II-based PEMCRs contain more PSS and less PAA units than copolymer I-based PEMCRs. TEM micrographs reveal that these PEMCRs can be used to synthesize not only goethite nanocrystals but also silver nanoparticles spontaneously and that the composition of two types of nanoparticles within the shell can be tuned. The average particle size of the goethite nanocrystals was 20 nm in width and 60−90 nm in length. Silver nanoparticles with an average size below 10 nm were formed in most cases. The difference in silver particle size was not significant between the PEMCRs after one and three reaction cycles. Although the morphology of capsules reacted one time showed the formation of folds and tiny creases formed during drying in Figure 4a and d, a relatively smooth morphology of capsules was observed in the case of the capsules reacted three times, as shown in Figure 4b,e. This may indicate that goethite nanocrystals grown further within the shell layer prevent folds and creases of the capsule. This phenomenon was also observed in SEM micrographs.

Synthesis of two types of nanoparticles and their composition within the shell were also confirmed by energy-dispersive X-ray (EDX) analysis. Figure 5a shows the successful synthesis of

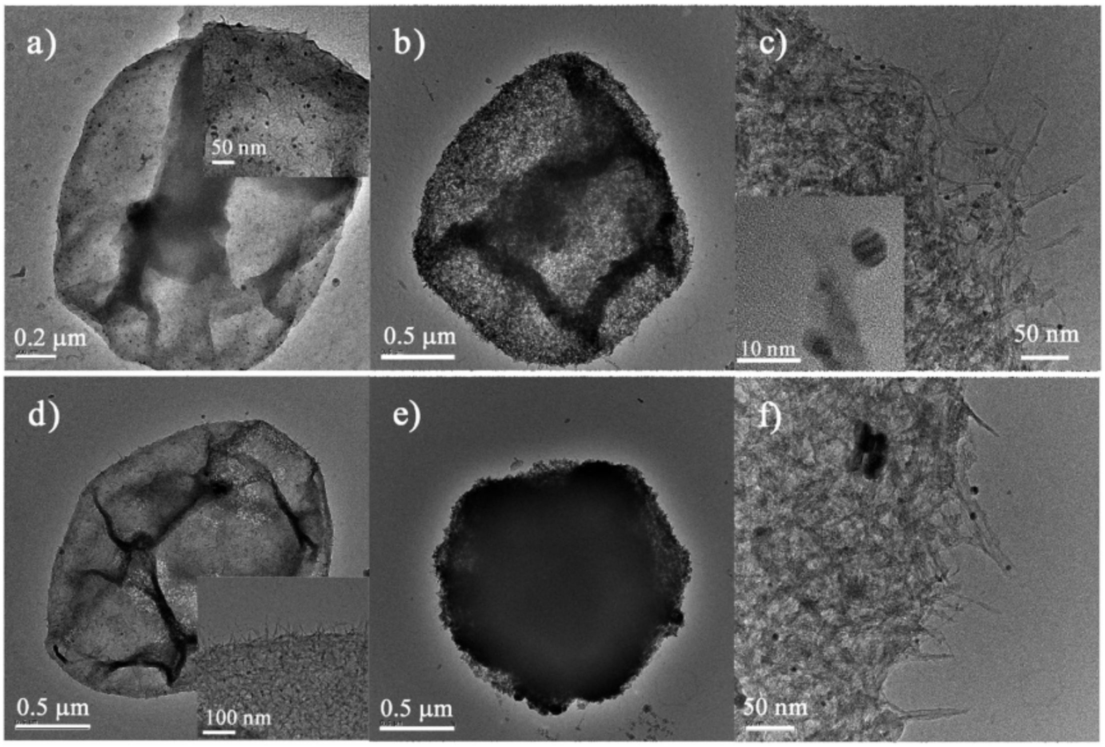
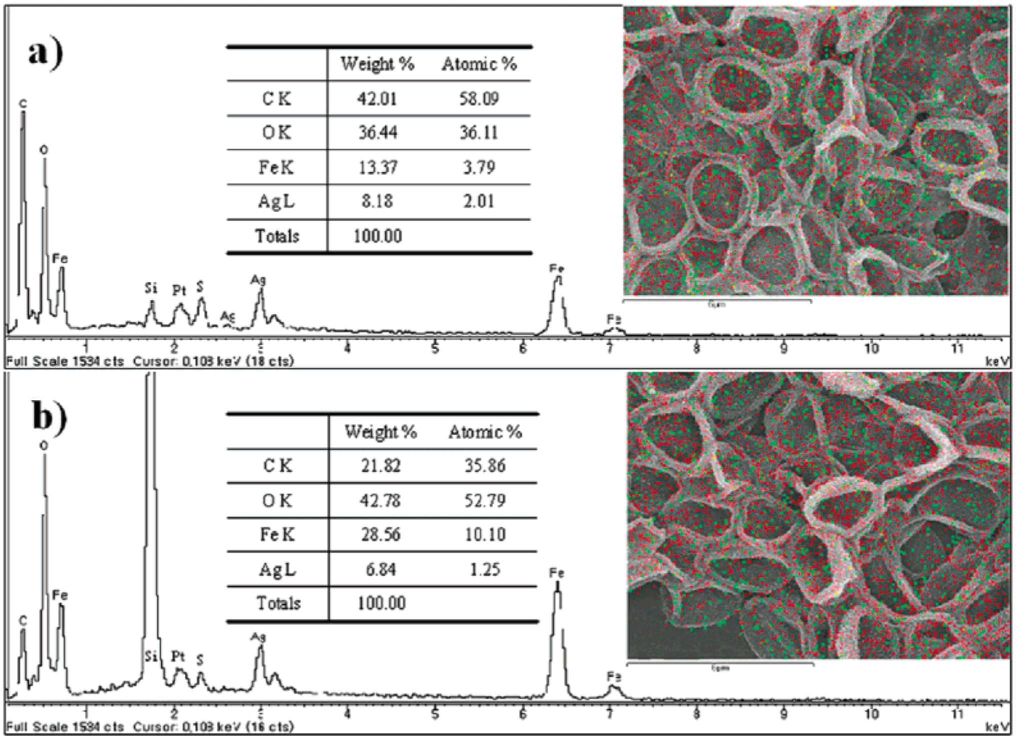


Figure 4. TEM micrographs of two types of nanoparticles within the shell of PEMCRs made from (a−c) copolymer I and (d−f) copolymer II, and after the different number of reaction cycles (a,d) one time, (b,e) three times. Panels (c) and (f) are magnified edge images of (b) and (e), respectively.



a)

	Weight %	Atomic %
C K	42.01	58.09
O K	36.44	36.11
Fe K	13.37	3.79
Ag L	8.18	2.01
Totals	100.00	

b)

	Weight %	Atomic %
C K	21.82	35.86
O K	42.78	52.79
Fe K	28.56	10.10
Ag L	6.84	1.25
Totals	100.00	

Figure 5. EDX analysis after the synthesis of two types of nanoparticles within (a) copolymer I- and (b) II-based PEMCRs. Mapping analysis reveals Ag from silver and Fe from goethite in the inset (red: Fe; green: Ag).

two types of nanoparticles of iron at 3.79% and silver at 2.01% (copolymer I, three reaction cycles). When copolymer II-based PEMCRs were used in the synthesis, the iron and silver contents were increased to 10.1% and decreased to 1.25%, respectively (Figure 5b). Synthesis of two types of nanoparticles within copolymer II-based PEMCRs provides more iron and less silver content than copolymer I-based PEMCRs due to the high PSS and low PAA contents within copolymer II. Additional evidence that confirms the tuning of the composition of two types of nanoparticles is their oxygen content. Although the carbon content was higher than the oxygen content in Figure 5a, the oxygen content was higher than carbon content in Figure 5b. This indicates that the concentration of goethite nanocrystals having two oxygen atoms was higher in the case of copolymer

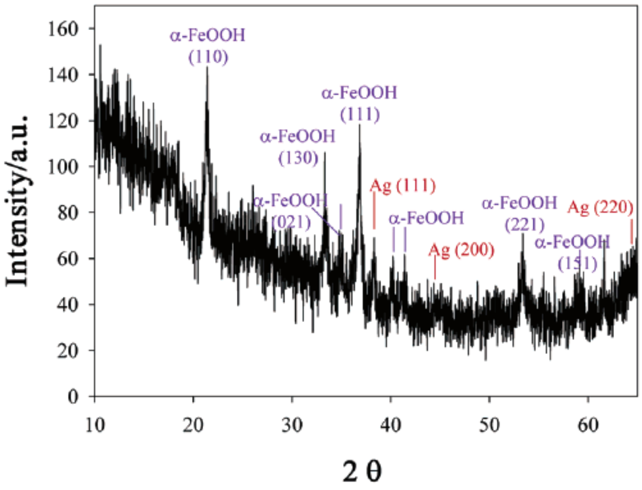


Figure 6. XRD pattern of goethite and silver-embedded PEMCs.

II-based ones. The amount of goethite nanocrystals synthesized within the shell was much higher than that for silver in both Figure 5a and b. It seems that iron ions attached to PAA after addition of silver ions could be replaced by silver ions, while iron ions for the synthesis of goethite could remain on the amine groups of PAH as well as sulfonate groups of PSS (Figure SI1 in the Supporting Information). EDX/mapping measurements also reveal that these specially designed PEMCRs can synthesize two types of nanoparticles spontaneously and that their composition can be tuned by varying the ratio of functional groups in the shell structure. To investigate the possibility of controlling nanoparticles composition in an opposite reaction sequence, two types of nanoparticles were synthesized within the PSS−PAA/PAH multilayers in the Ag−Fe reaction sequence. Figures SI2 and 3 in the Supporting Information show that the composition of two types of nanoparticles within the PSS−PAA/PAH multilayers also depends on the copolymer ratio even in the Ag−Fe reaction sequence. Mapping measurements were performed to visualize the distribution of two types of nanoparticles within the shell (inset in Figure 5). When $FeSO_4$ and $AgNO_3$ were used for the incorporation of Fe^{2+} and Ag^+ into the PEMC shell, goethite and silver nanoparticles were exclusively formed within the PEMCRs, and no free nanoparticles were found in the background. The identification of the goethite and silver nanoparticles was done via X-ray diffraction (XRD) measurements. Figure 6 shows an XRD pattern of two types of nanoparticle-embedded capsules (copolymer II basis), which is identical to pure goethite and silver. Both goethite and silver diffractograms were well matched with that of goethite and silver, obtained from a database, and no other peaks were detected.

Since these two types of nanoparticle-embedded PEMCs contain silver nanoparticles, antimicrobial activity could be expected. To investigate the antimicrobial activity of the PEMCs, *Escherichia coli* was employed as microorganism in an antimicrobial test. Figure 7 shows the antimicrobial activity of two types of nanoparticle-embedded capsules against an *Escherichia coli*. Optical density measurements quantitatively show the difference in turbidity, and absorbance at 260 nm[28] is proportional to the number of *Escherichia coli*. In the absence of goethite/silver-embedded capsules, the optical density of the *Escherichia coli* suspension was very high (inset (filled diamond) in Figure 7). After exposure of the *Escherichia coli* to goethite/silver-embedded capsules, the optical density of the *Escherichia coli* suspension dramatically decreased after 1 min as a result of cell death, and the *Escherichia coli* suspension became more transparent. In the presence of goethite-embedded capsules without silver, the optical density of the *Escherichia coli* suspension remained almost unchanged (inset and Figure 7 (nonfilled diamond)).

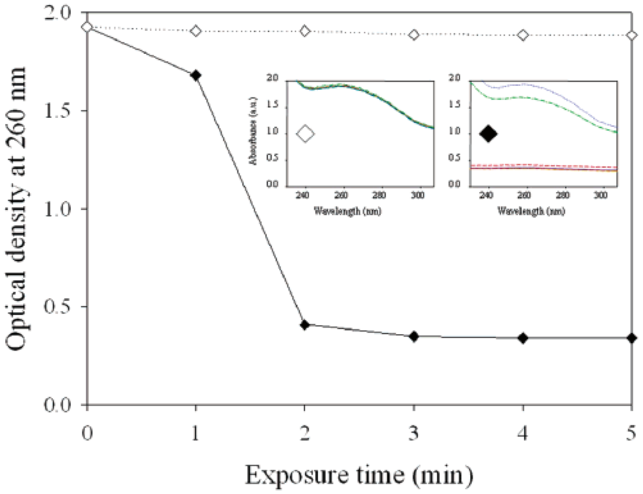


Figure 7. Optical density at 260 nm and spectra (inset) measured from suspension of *Escherichia coli* with silver/goethite-embedded capsules (filled diamond) or with goethite-embedded capsules (nonfilled diamond) as a function of exposure time.

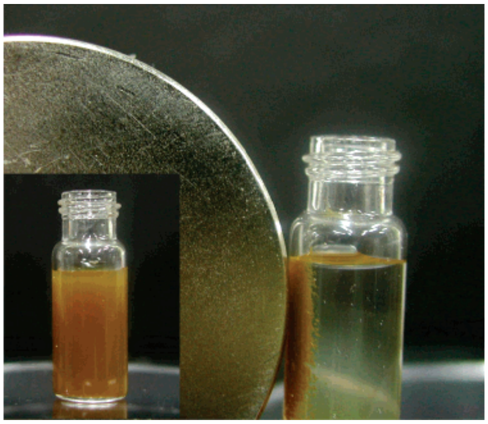


Figure 8. Photographs of the separation and redispersion process of magnetic PEMCs, with an external magnetic field, (inset) without an external magnetic field. A color change from ocher yellow to transparent was observed when an external magnetic field was applied.

Our PEMCs also contain magnetic goethite, therefore, positioning by an external magnetic field would be possible. Figure 8 illustrates the separation and redispersion process of magnetic PEMCs after the synthesis of two types of nanoparticles. In the absence of an external magnetic field, the dispersion of magnetic PEMC was ocher-yellow colored and homogeneous (inset in Figure 8). When an external magnetic field was applied, due to string attraction force to the magnet, these magnetic PEMCs were enriched only at the sidewall, and the dispersion became clear and transparent (Figure 8). This indicates that our goethite/silver-embedded PEMCs can be utilized as a position

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controllable antimicrobial carrier/protector by application of an external magnetic field.

Conclusions

In conclusion, we have demonstrated that both silver nanoparticles and goethite nanocrystals can be synthesized by means of novel PEMCRs with two different functional groups capable of synthesizing two types of nanoparticles. These PEMCRs enabled the composition as well as the amount of the loaded two types of nanoparticles within the shell of PEMCs to be controlled by the copolymer ratio and the number of reaction cycles. We also report that, due to their two types of nanoparticles and consequent dual functions, our specially designed PEMCs containing both silver and goethite nanocrystals can be used as antimicrobial capsules, which can be movable by an external magnetic field. The major advantage of our approach is that PEMC nanoreactor chemistry can be extended to the tunable synthesis of two types of nanoparticles within a single component system that possesses more than a single function.

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Supporting Information Available: EDX data after synthesis of nanoparticles within PEMCRs composed of PSS/PAH and PAA/PAH (Fe−Ag) and PSS/PAH, PAA/PAH, and PSS−PAA/PAH (Ag−Fe). This material is available free of charge via the Internet at http://pubs.acs.org.

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