Layer-by-layer (LBL) self-assembled polyelectrolyte multilayer (PEM) capsules are of scientific and technological interest for use as micro- and nanosized reactors, optical materials, and building components for nanoengineering owing to their controllable permeability and ease of surface functionalization.\(^1\)\(^-\)\(^10\) Shell of these capsules can be readily functionalized with various ions, functional molecules, and inorganic nanoparticles through electrostatic interaction. In particular, PEM capsules doped with gold nanoparticles (AuNPs) are attractive for many optical, biomedical applications because of strong plasmon resonance of AuNPs that can act as absorption antennas.\(^11\)\(^-\)\(^13\) For this reason, many efforts have been devoted to the preparation of PEM capsules functionalized with AuNPs. For example, Gittins and co-workers\(^14\) have prepared AuNP-doped PEM capsules by infiltration of the preformed AuNPs onto the PEM-coated colloidal template and subsequent removal of the cores, which allows the release of the encapsulated material on demand upon irradiation with laser light. In another study, AuNP-doped PEM capsules were used for enhanced Raman imaging and optical spectra.\(^15\) In our previous work, AuNPs were directly grown inside the PEM shells through electrostatic binding of Au precursor onto a PEM and subsequent chemical reduction.\(^16\)\(^,\)\(^17\)

Recently, interest in gold nanorods (AuNRs) has increased due to their optical response in the visible and near-infrared (NIR) region.\(^18\)\(^-\)\(^20\) AuNRs possess two absorption bands, one at a shorter wavelength (transverse plasmon resonance, around 520 nm) and the other at a longer wavelength (longitudinal plasmon resonance) that undergoes a bathochromic shift with increasing aspect ratio.\(^21\) Such versatile tunability of AuNR spectra in the NIR region would be attractive for many advanced applications. As for preparation of AuNRs, wet chemical synthesis protocol referred to as “seed-mediated growth” are well established by several groups.\(^22\)\(^-\)\(^24\) In this protocol, the cationic surfactant cetyltrimethylammonium bromide (CTAB) is used as a shape-inducing agent as well as a stabilizing agent of AuNRs. However, ready aggregation of AuNRs upon removal of the CTAB often prohibits application of as-synthesized AuNRs. To overcome this problem, modification of the surface of AuNRs with suitable materials including various polymers and inorganics were explored.\(^25\)\(^-\)\(^29\)

There are few reports about PEM capsules functionalized with AuNRs in comparison with that of AuNPs. As a rare example, Pastoriza-Santos et al. reported several studies on hollow capsules doped with AuNRs.\(^30\)\(^,\)\(^31\) They prepared AuNR–Silica capsules by successive coating of preformed AuNRs and silica onto polystyrene (PS) beads and the subsequent removal of the cores. In this case, surface passivation of AuNRs with polyvinylpyrrolidone (PVP) is required prior to adsorption onto PS beads for promoting stable complexation of AuNRs onto PS through electrostatic attraction.

In this report, we introduce a novel method for incorporation of AuNRs onto PEM capsules. Using seed-mediated growth of AuNRs in the presence of the preformed PEM capsules in the growth solution, direct growth of the AuNRs at the surface of the capsules, as well as stable complexation between the AuNRs and the capsules, was obtainable. The AuNRs could also be combined with silica-coated PEM capsules (PEM–Silica capsules), which would potentially improve the stability of the capsules. These capsules show tunable optical properties as a function of the aspect ratio of the AuNRs synthesized. By this method, AuNRs could be immobilized onto the PEM capsules or the PEM–Silica capsules without aid of prior surface modification of the AuNRs. Because the PEM capsules acted as solid supports for the adsorbed AuNRs, the optical properties of the resulting composite capsules were more stable upon repetitive washing than the freely suspended AuNRs. To the best of our knowledge, this is the first report of direct growth of optically stable AuNRs on PEM capsules.

An overall schematic for the growth of AuNRs on the PEM capsules and the PEM/Silica capsules is shown in Figure 1. The PEM capsules were prepared by LBL assembly of poly(styrene sulfonate) (PSS) and poly(allylamine hydrochloride) (PAH) onto weakly cross-linked melamine-formaldehyde (MF) particles and subsequent removal of the MF core by treatment with HCl. In total, nine layers of PEMS with a PSS outmost layer were used to fabricate the PEM capsules. To fabricate the PEM–Silica capsules, the PEM capsules were directly coated with silica by Stöber method, in which a tetraethylorthosilicate (TEOS) was used as the silica precursor.\(^32\) About 50 nm thickness of the silica was typically
obtained under our experimental conditions. After preparation, the PEM or PEM–Silica capsules were exposed to the growth solution for synthesis of AuNRs. The AuNRs were synthesized in solutions by the seed-mediated growth reported by Murphy and co-workers. In this method, silver nitrate was used for synthesis of aspect ratio-controlled AuNRs in very high yield. The capsules were added immediately before the seeding step, and AuNR growth was initiated by adding specific quantities of the seeds into the growth solution.

Figure 2 shows the TEM images of the PEM capsules and the PEM–Silica capsules before and after synthesis of the AuNRs. In case of the PEM–Silica capsules, the presence of silica increased the mechanical strength and robustness of the capsules, thus the spherical shape of the capsules was preserved after solvent evaporation (Figure 2b). Because we removed the MF core first then coated silica onto the PEM capsule, shape deformation or rupture of the silica shell upon removal of core at the final stage could be avoided. For both the PEM capsules and the PEM–Silica capsules, the AuNRs were successfully grown and formed stable complex with the capsule structures (Figure 2c and 2d). With this approach, we could prepare variety of capsules by changing the template size and the aspect ratio of the AuNR synthesized in the capsules.

It is noteworthy that preformed AuNRs hardly adsorb to the PEM or PEM–Silica capsules. The PEM and PEM–Silica capsules were negatively charged in aqueous solution owing to the presence of sulfonate groups and deprotonated hydroxyl groups on their surface, respectively. As-synthesized AuNRs are known to be positively charged because of the presence of the bilayer of CTAB on their surface. Thus, electrostatic attraction between the AuNRs and the PEM or PEM–Silica capsules could be anticipated; however, they were not found in this case. In case of the reaction between preformed AuNRs and the PEM or PEM–Silica capsules, almost no AuNRs were adsorbed after prolonged reaction (see Figure S1, Supporting Information). There are at least two possible explanations for this unfavorable interaction between as-synthesized AuNRs and the capsules used in this study: 1) Although some portion of the AuNRs are adsorbed onto the capsule surface through electrostatic attraction, they are easily detached from the CTAB layers upon further reaction or washings because of the noncovalent, vulnerable Au–N bond between AuNRs and CTAB bilayers. 2) Freely suspended CTABs in the AuNR solution would adsorb to the surface of the PEM or PEM–Silica capsules in the form of bilayers. Therefore, the following charge reversal of the capsules from negative to positive charge would exert repulsive force on the AuNRs, inhibiting adsorption of the AuNRs on the PEM or PEM–Silica capsules. The charge reversal of the capsules upon exposure to the CTAB solution was examined through the measurement of the zeta potentials of the capsules. The measured zeta potential values for the PEM and PEM–Silica capsules after being exposed to the CTAB solutions were $47.88 \pm 2.23$ mV and $53.3 \pm 0.82$ mV, respectively (before exposure: $-28.25 \pm 0.91$ mV and $-2.03 \pm 0.32$ mV, respectively). This charge reversal of the capsule after exposure to the CTAB solution may hinder adsorption of preformed AuNRs on the PEM or PEM–Silica capsules. Therefore, the following charge reversal of the capsules from negative to positive charge would exert repulsive force on the AuNRs, inhibiting adsorption of the AuNRs on the PEM or PEM–Silica capsules. The charge reversal of the capsules upon exposure to the CTAB solution was examined through the measurement of the zeta potentials of the capsules. The measured zeta potential values for the PEM and PEM–Silica capsules after being exposed to the CTAB solutions were $47.88 \pm 2.23$ mV and $53.3 \pm 0.82$ mV, respectively (before exposure: $-28.25 \pm 0.91$ mV and $-2.03 \pm 0.32$ mV, respectively). This charge reversal of the capsule after exposure to the CTAB solution may hinder adsorption of preformed AuNRs, but it can be helpful for our direct growth of AuNRs onto the capsules. Because growth of the AuNRs can be readily initiated on the surface of the capsules covered with the CTAB bilayers, the following AuNRs grown on the surface of the capsules can be more stably fixed onto the capsules.

To investigate the optical properties of the resulting capsules, UV-vis absorption spectra were acquired (Figure 3). They showed two main absorption maxima, the first located around 520 nm and the second located in the longer wavelength corresponding to the characteristic of rod-shaped nanogold. Also, there is a weak plasmon band in between the two major bands that can be attributed to the complexation of small portion of the nonrod-shaped AuNPs onto the capsules. Because both the PEM and the thin silica shell are transparent in this region, the overall spectra are dominated by the two characteristic plasmon bands of AuNRs. Analogous to
free AuNRs, aspect ratio of the AuNRs grown on the capsules can be easily tuned by the amount of the reactants used. Figure 3b shows the variance of the longitudinal plasmon band of the resulting PEM capsules upon variation of the amount of silver nitrate. For a given amount of gold, as the amount of the silver nitrate (0.01 M) varies from 0.01 mL to 0.06 mL, the average aspect ratio of the AuNRs synthesized within the capsules varies from 2.86 to 3.45 with average longitudinal plasmon maximum from 669 nm to 781 nm. By controlling the amount of silver nitrate, we could control the aspect ratio of the AuNRs along with improved yield, as previously reported.[39]

Because the AuNRs are stably complexed to the PEM matrix, the PEM capsules can act as a support to prevent aggregation of the AuNRs. It is known that a colloidal stability of as-synthesized AuNRs is conditioned to the presence of minimum amount of CTAB molecules in the solution.[33] Repetitive washing cause irreversible aggregation of free AuNRs by excessive removal of CTAB in solution. However, our AuNR/capsule composites showed relatively stable optical property upon washing. As shown in Figure 4a, free AuNRs start to severely aggregate when washes with water 3 times. In comparison, our AuNR-loaded capsules showed relatively stable optical property upon repetitive washing up to seven times (Figure 4b). A recent report explored the cytotoxicity of the CTAB-stabilized AuNPs.[40] It was found that toxicity was because of free CTABs in solution but not because of the CTAB bound to the nanoparticles. Therefore, we believe this aggregation-resistant property of our AuNR-loaded capsules could be an alternative way to enhance colloidal stability of AuNRs without deterioration of the optical properties of AuNRs.

In conclusion, we demonstrated a facile preparation of interesting type of new composite capsules, based on the direct growth of AuNRs onto the PEM-layered capsules. Our method illustrates a new route to capsule structures that are readily functionalized with AuNRs and would be difficult to prepare by other existing methods. The resulting capsules showed NIR absorbing property like as freely AuNRs in solution, with tunable optical properties that depend on the aspect ratio of the grown AuNRs. Modification of the method can lead to formation of multiple types of capsules combining diverse types of shells and nanoparticles or nanorods. The resulting capsules showed greater optical stability than the freely suspended AuNRs in solution. This novel fabrication method for incorporation of the AuNRs onto the PEM or PEM–Silica capsules would be useful for many applications where optically active materials based on organic–inorganic hybrid nanostructures are needed.

**Experimental Section**

Preparation of PEM capsules and PEM–silica capsules: PSS and PAH (1.4 mL, 2 mg mL\(^{-1}\) solution) were alternately adsorbed
on the MF particles (5 wt% 0.12 mL, 590 nm) for 15 min. In between the PE adsorption, centrifugation/washing/redispersion cycles were repeated. In total, nine PEMs were deposited on the MF particles. PEM capsules were obtained by decomposing MF cores with 0.15 M HCl solution (pH < 1). For preparation of PEM-Silica capsules, the PEM capsules were dispersed in a solution containing 1 mL of 2-propanol, 0.18 mL of water, and 0.025 mL of NH4OH. The resulting solution was stirred vigorously for 30 min after the addition of 30 μL tetraethyloxysilicate (TEOS), which resulted in the formation of silica shell with thickness of 50 nm outside the PEM capsules.

**Gold nanorod growth on PEM capsules or PEM–silica capsules:** Gold seeds and nanorods were prepared using a wet-chemical method similar to the method described by Sau et al. In a typical experiment, 4.75 mL of 0.10 M CTAB, 0.20 mL of 0.01 M HAuCl4·3H2O, and 0.03 mL of 0.01 M AgNO3 solutions were added in that order, to a test tube, followed by gentle mixing. Then 0.032 mL of 0.10 M AA was added to it. The solution became colorless upon addition and mixing of AA. Finally, 0.1 mL of the PEM capsules or PEM–silica capsules (0.01 wt%) and 0.01 mL of seed solution were added, and the reaction mixture was gently mixed for 10 s and left undisturbed for at least 3 h.

**Characterization:** Absorption spectra of the capsules containing gold nanorods were taken on a Cary 1E (Varian) spectrophotometer. FE-TEM measurements were performed on a Philips (Tecnai F20) microscope operating at 200 kV. The surface charge potentials of the CTAB-capped PEM capsules formed on a Philips (Tecnai F20) microscope operating at 200 kV. UV-vis-NIR spectrophotometer. FE-TEM measurements were performed on a Cary 1E (Varian) spectrophotometer. FE-TEM measurements were performed on a Philips (Tecnai F20) microscope operating at 200 kV.

**Keywords:** microcapsules, nanocomposites, nanorods, nanostructures, polyelectrolytes

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