Materials Science

"Grafting-From" Polymerization inside a Polyelectrolyte Hollow-Capsule Microreactor**

Won San Choi, Jeong-Ho Park, Hye Young Koo,
*Ju-Young Kim, B. K. Cho, and Dong-Yu Kim**

Over the last decade versatile, electrostatic layer-by-layer (LbL) assembly methods involving polyelectrolytes[1–5] have been widely used in the preparation of hollow capsules. These capsules can be fabricated by the stepwise adsorption of polyelectrolytes with charges that are opposite from their aqueous media onto templating cores, especially organic or inorganic particles and biopolymers,[6] followed by dissolution of the templating cores to give polyelectrolyte hollow capsules that are replicas of the templates.[7–10]

A variety of microcapsules with customized physicochemical properties can be produced by incorporating one or more functional components, such as nanoparticles, biomacromolecules, lipids, photosensitive dyes, inorganic crystals, and multivalent ions, onto the capsule wall or into the interior of the capsule.[11–15] Hollow capsules consisting of alternating layers of strong and weak polyelectrolytes can also be used for the targeted encapsulation and controlled release of macromolecules by tuning the porosity upon changing the pH value.[16,17] Most of these studies have focused on the development of synthetic methodologies and the characterization of the hollow capsules. Relatively little attention has been directed to reactions in the confined interior of these hollow capsules.[18–20] In these studies, hollow capsules were used as microreactors for spatially restricted inorganic synthesis. However, only a limited number of reports have appeared that demonstrate that polymerization inside hollow capsules could provide new opportunities for tuning the properties of the products. For example, polyelectrolyte-loaded capsules have been used to tune the physicochemical properties of the products formed in the interior of a nanoreactor capsule,[21,22] and enzyme-loaded capsules have been employed for the synthesis of polymers within microcapsules.[23,24]

Recently, the so-called "grafting-from" polymerization technique has attached a great deal of attention because polymer brushes can be generated with high grafting densities of surface-attached neutral macromolecules, as well as polyelectrolytes.[25–27] Grafting-from polymerization at solid surfaces can be performed directly at the surface by using an immobilized initiator and various polymerization techniques. The initiator system is immobilized on the surface of a solid substrate and the polymer layer is then generated by polymerization in situ. To date, these grafting-from polymers or polymer brushes have been largely prepared on flat substrates.

Herein we report the grafting-from polymerization to generate end-attached polyelectrolyte brushes inside a hollow-capsule microreactor. To the best of our knowledge, polymer brushes grown from the inner wall of hollow capsules have not yet been reported. This novel fabrication method for hollow capsules was performed by preparing polyelectrolyte hollow capsules whose inner layer was coated with a water-soluble initiator, followed by polymerization of a styrene sulfonate (SS) monomer on the inner wall. The shape of the capsules after polymerization could be controlled by varying the SS content. Furthermore, we also demonstrate that these hollow capsules can be used as a novel submicroreactor to control polymerization behavior.

Figure 1 shows the fabrication of polyelectrolyte hollow capsules with initiator bound on the inner wall, and the grafting-from polymerization. Poly(allylamine hydrochloride) (PAH) and poly(styrene sulfonate) (PSS) were used as the positive and negative polyelectrolytes, respectively, and potassium peroxodisulfate (KPS) was used as the water-soluble initiator. The capsule reactors were fabricated by the layer-by-layer (LbL) assembly technique[28–30] on sacrificial

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[*] W. S. Choi, J.-H. Park, H. Y. Koo, J.-Y. Kim, Prof. B. K. Cho,
Prof. D.-Y. Kim
Center for Frontier Materials
Department of Materials Science and Engineering
Gwangju Institute of Science and Technology
1 Oryong-dong, Buk-gu, Gwangju 500-712 (Korea)
Fax: (+82) 62-970-2304
E-mail: kimdy@gist.ac.kr

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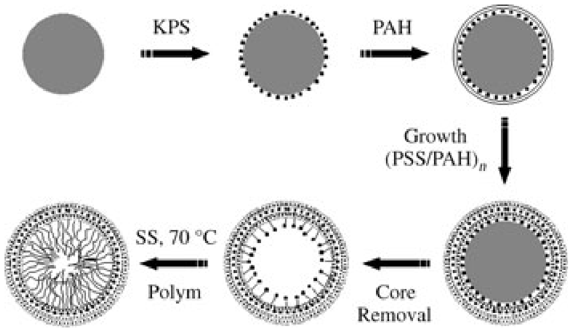


Figure 1. Schematic representation of the procedures used for fabricating initiator-coated hollow capsules and grafting-from polymerization inside the capsules.

colloidal particles, followed by decomposition of the cores in HCl solution. The amount of initiator bound onto the capsules was estimated to be about 57 % of the original amount by measurement of the amount of free initiator extracted. The water-soluble monomer styrene sulfonate (SS) was subsequently dispersed in a suspension of initiator-bound hollow capsules. PSS was then grown by a grafting-from polymerization method at 70 °C for four hours. The SS monomers are selectively polymerized inside the capsule reactors only, because the initiator is present only at the inner wall of the hollow capsules. After polymerization, the immobilized polymers bound to the interior of the hollow capsules were released by treatment with HCl to characterize them further. Figure 2 summarizes the ζ potential recorded with layer deposition for the KPS(PAH/PSS)$_2$PAH system. The ζ potential alternates between positive and negative values, thereby indicating the successful recharging of the particles coated with the polyelectrolyte layers after deposition of each layer.

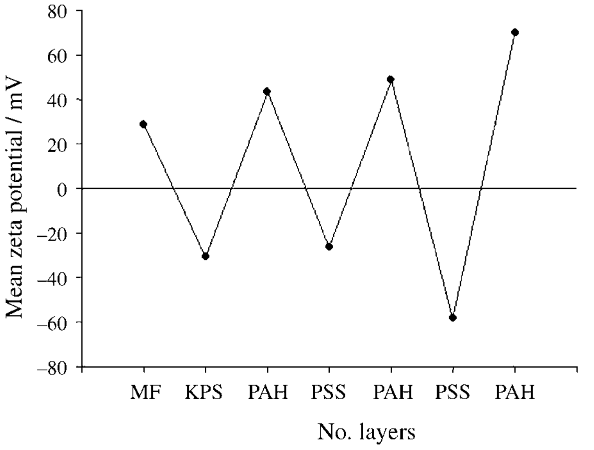


Figure 2. ζ potential as a function of layer number for MF particles coated with KPS(PAH/PSS)$_2$PAH. Experiments were repeated three times for each measurement and the average value was used. The line shown is to guide the eye and has no other meaning.

To confirm the immobilization of KPS at the inner wall of the hollow capsules the temperature-dependent magnetization of the hollow capsules with and without KPS was measured with a superconducting quantum interference device (SQUID) magnetometer: the generation of radical species arising from the dissociation of KPS would allow the detection of a change of magnetization. As shown in Figure 3, while no change in magnetic moment was observed between 300 and 340 K for the hollow capsules without KPS, a sudden jump in magnetization was observed at 322 K for the hollow capsules with KPS, which is close to the typical initiation temperature of KPS. These observations mean that radical species–-unpaired electrons—are produced upon dissociation of KPS, and that these species subsequently propagate. Therefore, the detection of magnetization is direct evidence that KPS is bound to the inner wall of the hollow capsules and could play a role as a polymerization initiator.

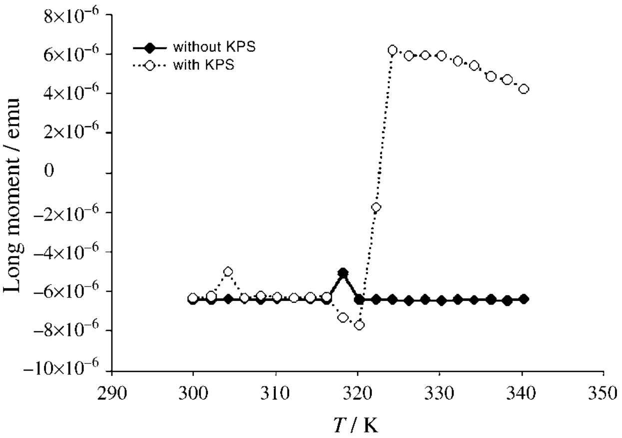


Figure 3. The SQUID measurements of hollow capsules without and with KPS in a solution with SS monomer. The latter case shows a dramatically increased magnetic moment at 320 K as a result of activation and propagation of the KPS initiator, whereas the former case does not.

Figure 4 shows SEM micrographs of the polyelectrolyte-coated particles and the corresponding hollow capsules obtained after removing the melamine formaldehyde (MF) core and drying on a silicon wafer. The drying process forms creases and folds in the shells as they collapse. Essentially no residual MF could be detected by SEM.

These hollow capsules were dispersed in a solution of the SS monomer. The polymerization was carried out with different SS contents at 70 °C for four hours. After the polymerization, the capsules were separated from the solution of the SS monomers by centrifugation; their shapes were found to be dependent on the initial SS content. Figure 5 shows SEM micrographs of hollow capsules after polymerization in solutions containing 25 wt % (Figure 5 a) and 40 wt % (Figure 5 b) of SS monomer. The latter shows "semispherical" capsules because sufficient polymers (PSS) have been produced to fill the capsules, whereas the former shows "caved-in" capsules as a result of insufficient amounts of polymer inside the capsules. The size of the "caved-in" and "semispherical" capsules is about 600 and 800 nm, respectively.

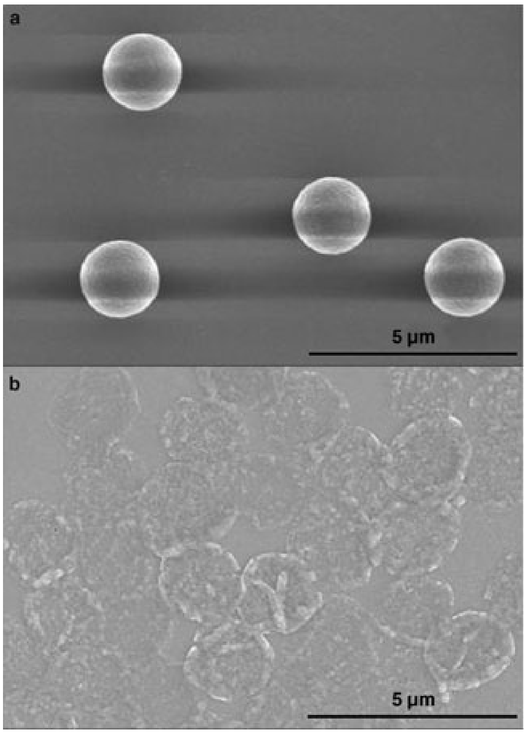


Figure 4. SEM micrographs of a) an MF particle coated with KPS/(PAH/PSS)$_2$PAH, and b) the corresponding hollow shell obtained after removal of the MF core by treatment with HCl.

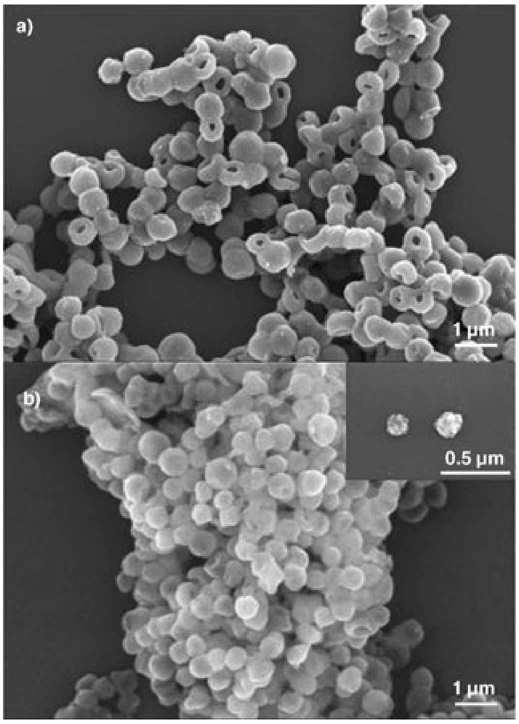


Figure 5. SEM micrographs of the polymer-containing capsules: a) "caved-in" capsules (25 wt% SS monomer); b) "semispherical" capsules (40 wt% SS monomer). Hollow capsules without SS monomer undergo severe shrinkage at 70 °C (inset).

The hollow capsules shrink after polymerization: their size was reduced from a diameter of 1.87 µm to about 200 nm after heating to 70 °C for four hours in the absence of SS monomer (inset in Figure 5). It has been reported that heating can cause shrinkage of the surface area by 20% leading to a reduction in the diameter of the capsules and an increase in wall thickness as a result of the breaking and re-forming of ion pairs, thus yielding a more three-dimensional configuration of the polymer.[7] In our case, the shrinkage is more severe because of the prolonged heating and the thinner polyelectrolyte walls and indicate that the higher the monomer content the less the shrinkage of the capsules. It seems that the polymer chains on the interior of the capsule walls play an important role as a shrinkage-resistant framework. The shape of the "caved-in" particles is similar to that of erythrocytes, and these types of "caved-in" particles are known to show excellent properties when used as a plastic pigment in paper coating. The high-shear viscosity of the "caved-in" particles is lower than that of a spherical particle, and their sheet gloss, print gloss, and opacity are higher than those of spherical particles because of their shape.[31]

Field-emission transmission electron microscopy (FE-TEM) measurements were performed to examine the interior structure of the polymer-grown capsules. In the case of the "caved-in" capsules, the dark ring region corresponds to a polymer brush shell structure. The FE-TEM image of the "caved-in" case clearly shows hollows in the capsules, and, as expected, the semispherical case (Figure 6 b and 6 d) shows no evidence of a hollow. The FE-TEM analysis clearly reveals that the polymer brushes grow from the inner surface of the hollow capsules and are bound to the interior of the hollow capsule where they act as a shrink-resistant frame. It has been reported that the capsule shape can be stabilized by the formation of an insoluble, stiff, gel-like structure in the capsule interior which contains residual MF and PSS.[32] In our case, however, the capsule shapes are stabilized by the soluble polymers grown from the inner wall, and the shapes are

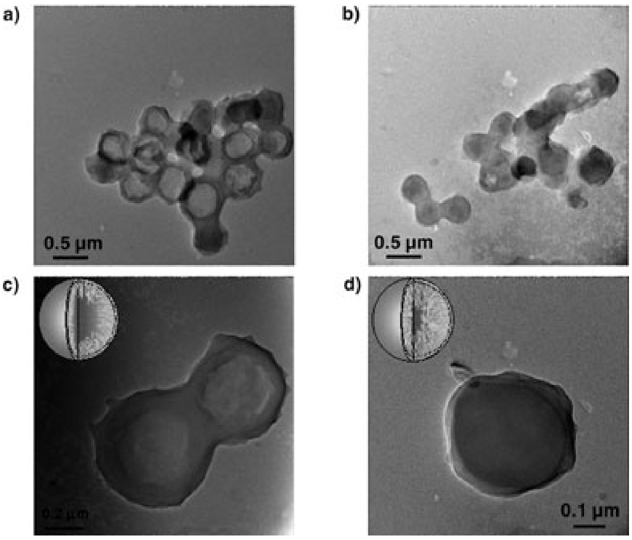
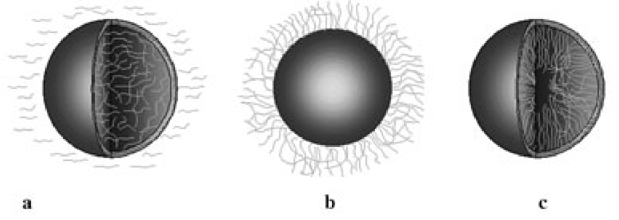


Figure 6. TEM micrographs of polymer-containing capsules as a function of monomer content: a), c) "caved-in" capsules (25 wt% SS monomer); b), d) "semispherical" capsules (40 wt% SS monomer).

determined by the amount of polymer present inside the capsules.

We also investigated the influence of the confined interior of our hollow capsules on the detailed polymerization behavior. Although polymerization behavior, such as the molecular weight and molecular-weight distribution of the polymers formed, in a bulk reaction space has been extensively investigated both theoretically and experimentally over a long period of time, there are only a few, limited methods available for controlling the polymerization behavior of common monomers. It would therefore be significant for the field of polymerization if such behavior could be manipulated by easily controllable factors, such as the confining geometry. We used our initiator-bound hollow capsules to investigate whether the confined nanospace and surface anchoring could be used to control the polymerization behavior. To do so, we polymerized PSS by using four different approaches to form "floating-outside" polymers, which are obtained from free-floating initiators outside the hollow capsules, "floating-inside" polymers, which are obtained from free-floating initiators inside the hollow capsules, "immobilized-outside" polymers, which are grown from the outer surface of highly cross-linked MF particles, and "immobilized-inside" polymers, which are grown from the inner surface of the capsules. The floating and immobilized polymers were collected after treatment with HCl. Polyelectrolyte shells are semipermeable,[28–30] and therefore small molecules such as an initiator and a monomer can easily penetrate through the shell wall, while large molecules, such as polymers, cannot. However, even large molecules can penetrate the shell wall when the polyelectrolyte shell has an open form, such as under acid conditions.[17] Thus, treatment with 0.5 M HCl permitted the interior polymers to be collected by opening the shell. After this treatment, the capsules were separated from the dangling polymer by centrifugation. Figure 7 shows a comparison of the molecular weights of the four types of polymers obtained inside and outside of the hollow capsules; 40 wt % of SS monomer was used in all cases. The floating-inside polymers have a molecular weight and PDI that are about twice those of the floating-outside polymers. This result indicates that some confined-space effects may exist. However, surprisingly, the immobilized-inside polymers grown from the inner surface have a molecular weight that is an order of magnitude higher than both the floating-inside and the floating-outside polymers. This kind of unusual polymerization behavior inside small capsules has not been reported until now.

To investigate the immobilization effect, SS monomers were polymerized on an initiator-bound MF surface. Highly cross-linked MF particles were used in this case. These immobilized-outside polymers have a higher molecular weight than the floating-outside polymers, but the difference is not as much as between the immobilized-inside and floating-inside cases (Figure 7b). Thus, the immobilization effect alone cannot explain the unusually high molecular weight of the immobilized-inside polymers. Even though the detailed mechanism responsible for this behavior is not yet clear, on the basis of the results described above we believe that this extraordinary molecular weight behavior results from *both immobilization and confined-space effects*. A further detailed examination of these effects is currently under way. We also expect that this kind of polymerization behavior could be further controlled by varying the capsule size. If this can be achieved, it might open up a new route to the development of "tunable microreactors", which could control a variety of chemical and polymerization reactions.



	M_n [Da]	M_w [Da]	PDI
PAH (hollow capsule basis)	10 452	12 463	1.19
PSS (hollow capsule basis)	30 895	64 057	2.09
floating-outside polymers (a)	28 863	44 662	1.54
floating-inside polymers (a)	59 195	147 583	2.49
immobilized-outside polymers (b)	37 639	76 414	2.03
immobilized-inside polymers (c)	515 480	1 361 527	2.64

Figure 7. Schematic representation and comparison of molecular weights and polydispersity index (PDI) of a) floating-outside and floating-inside polymers, b) immobilized-outside polymers obtained on a colloidal surface, and c) immobilized-inside polymers obtained in a confined space.

In conclusion, the hollow capsules reported here serve as a microreactor for the efficient polymerization of SS monomers in grafting-from polymerization inside the capsules. The hollow capsules formed after the grafting-from polymerization show either caved-in or semispherical shapes. The shape of the capsules after polymerization is strongly dependent on the initial SS content, thus implying the possibility to control the shape of the resulting nanoparticles in our system. The immobilized polymers obtained in the confined space have a much higher molecular weight than polymers produced in bulk solution as a result of both immobilization and confined-space effects. Thus, the polyelectrolyte hollow capsules reported here successfully serve as a unique microreactor for the polymerization and also allow the manipulation of the shape of the nanoparticles.

Experimental Section

PSS ($M_w = 70000$), PAH ($M_w = 15000$), KPS, and SS monomer were purchased from Aldrich. Weakly and highly cross-linked MF particles were purchased from Microparticle (GmbH) and Fluka, respectively. 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. The capsule reactors (KPS (2.3 mg)/(PAH (1 mg mL^{-1})/PSS (1 mg mL^{-1}))$_2$/PAH) were fabricated by the LbL assembly technique[28–30] on MF (0.12 mL) colloidal particles with a diameter of 1.87 μm, followed by decomposition of the MF cores in 0.15 M HCl solution (pH < 1). The detailed procedure for the formation of initiator-bound hollow capsules is as follows: an aqueous KPS solution (2 mL, 2.3 mg in water) was added to an aqueous suspension (0.12 mL) of positively charged MF particles (10 wt%). The dispersion was gently agitated for 15 min to allow the KPS to adsorb onto the MF particles. The mixture was then centrifuged at 10000 g for 4 min, the supernatant removed, and water (2 mL) added. The particles were then redispersed by gentle shaking. The centrifugation/wash/dispersion cycle was repeated three times to ensure removal of any free KPS from the solution. After formation of the KPS layer outside the MF cores, PAH and PSS polyelectrolyte layers were deposited by an established LbL assembly technique.[28–30] The polyelectrolyte assembling conditions, including the centrifugation/wash/dispersion cycle, were the same as described above (1 mg mL^{-1}, 0.5 M NaCl). After deposition of five layers of polyelectrolytes, the template MF core was removed by treatment with 0.15 M HCl (pH < 1) to give initiator-bound hollow capsules.

For the estimation of the amount of KPS initiator bound to the inner wall of the capsules, free initiator molecules were extracted and quantified follows: an aqueous solution of KPS (2.3 mg in 2 mL of water) was added to an aqueous suspension (0.12 mL) of positively charged MF particles (10 wt%). After adsorption of the KPS onto the MF particles, the dispersion was centrifuged, the supernatant containing free KPS collected, and water (2 mL) added. The particles were then redispersed by gentle shaking. The centrifugation/wash/dispersion cycle was repeated several times to ensure collection of the free KPS from the solution. The collected solution of free KPS was evaporated and the weight of the residue was measured. For each measurement, experiments were repeated five times and the average value was used. The measured weight was about 1 mg; therefore, the approximate amount of initiator bound to the MF cores was about 1.3 mg (57% of the original amount).

The water-soluble monomer styrene sulfonate (SS; 40 wt%, 44 mg) was subsequently dispersed in a suspension (1.5 mL, 0.03 wt%) of the initiator-bound hollow capsules. 25 and 40 wt% SS, relative to the MF emulsion weight, was used as the monomer. Polymerization was carried out at 70°C for 4 h.

Floating-inside and floating-outside polymers obtained from free-floating initiators inside and outside the hollow capsules were polymerized under the same conditions as described above; 40 wt% of SS monomer (44 mg) and KPS (2.3 mg) were dispersed in a suspension of the hollow capsules. Immobilized-outside polymers were obtained on the initiator-bound MF surface; a solution of KPS (2 mL) was added to an MF suspension (0.12 mL). The KPS adsorption procedure was the same as described above. After adsorption, the particles were separated from the KPS solution by centrifugation, followed by several washing cycles with water. SS monomer (40 wt%, 44 mg) was dispersed in a suspension (1.5 mL, 1.5 wt%) of KPS-bound MF particles. Polymerization was carried out under the same conditions as described above. For separation of all these polymers from the capsules the particles were dispersed in 0.5 M HCl for 20 min to allow the collection of the polymers. The dangling polymers (immobilized-inside and immobilized-outside) were collected by gently stirring the dispersion for 20 min and then centrifugation at 10000 g for 4 min. Finally, the supernatant containing the polymerized PSS was collected. To collect floating-outside polymers, the suspension containing the polymers was centrifuged in an aqueous medium and the supernatant containing the polymers was collected. To collect floating-inside polymers, the suspension containing the polymers was centrifuged in an aqueous medium and then the precipitate was dispersed in 0.5 M HCl for 20 min; the collection process was the same as described above.

The surface charge was measured on an OTSUKA (ELS 8000) apparatus. The FE-SEM micrographs were obtained with a Hitachi (S-4700) microscope. The FE-TEM measurements were performed on a Philips (TECNAI F20) microscope operating at 200 kV. Samples were prepared by applying a drop of the capsule solution onto a carbon-coated copper grid. The molecular weights and their PDI values were measured by gel-permeation chromatography (GPC, Breeze System 500 Series). SQUID measurements were performed on a Quantum design (MPMS XL) device with scan temperatures from 300 K to 340 K at 10 K min^{-1} in 2 K increments (21 steps).

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