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Two-Dimensional Self-Assembly of Spherical Particles Using a Liquid Mold and Its Drying Process

Y. Masuda,* K. Tomimoto, and K. Koumoto

*Department of Applied Chemistry, Graduate School of Engineering, Nagoya University,
Nagoya 464-8603, Japan*

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We developed a novel process to fabricate particle wires through self-assembly on hydrophilic regions of SAMs (self-assembled monolayer). A SAM of octadecyltrichlorosilane was formed on a silicon substrate and modified by UV irradiation to create a pattern of hydrophobic octadecyl and hydrophilic silanol groups. Ethanol or water containing particles (550 or 800 nm diameter) were dropped onto a patterned SAM. The solution was separated into two droplets with a liquid bridge between the droplets along the hydrophilic regions of a patterned SAM. The droplets and the liquid bridge were used as a mold for fabrication of a two-dimensional pattern of colloid crystals. Particle wire was formed between two droplets and colloid crystals such as an opal structure were formed at both ends of the particle wire after drying the solution. The particle wires constructed from a close-packed structure or non-close-packed structure, i.e., square lattice, were fabricated through self-assembly at room temperature using this method.

Introduction

Particles show various interesting properties¹ that are not observed in the bulk form of a material. Recently, monodispersed particles have been synthesized by various methods. Thus, particles may be treated as if they were atoms, and one-, two- or three-dimensional arrangement of particles have been studied by many researchers. For instance, photonic crystals can be constructed by monodispersed particles. Additionally, electronic energy transfer in close-packed CdSe² or InP³ quantum dots arises from dipole–dipole interdot interactions between proximal dots.^{4,5} To apply these novel properties for future devices,

precise particle arrangement techniques to produce desired particle assemblies must be developed.

Natural opal constructed from close-packed particles, i.e., face-centered cubic (fcc) structure, is formed by sedimentation of microparticles. A close-packed structure is also prepared artificially by several techniques^{6–9} such as electrophoretic deposition,⁶ flow of colloidal solution through a mold with microdrains,⁷ and a three-layer technique.⁸ Furthermore, many assemblies of particles were fabricated.^{10–13} A hollow sphere was prepared from

* To whom correspondence may be addressed. Tel: +81-52-789-3329. Fax: +81-52-789-3201. E-mail: masuda@apchem.nagoya-u.ac.jp (Y. Masuda).

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particles using emulsion droplets,¹⁰ a monoparticle shell or particle helix was prepared using templates such as a large core particle or a tubule, respectively,¹¹ islands of Ag₂S nanoparticles, which show the {100} plane of the fcc structure, were prepared from colloidal solution,¹² and quasi-one-dimensional chains of Au nanoparticles were prepared using an alumina membrane.¹³ Additionally, particle layers were formed on substrates by several methods.^{8,14–25} Layering of Au particles was realized by a casting method^{14,15} at first. Electrostatic interaction was also used for assembly and alternate adsorption of Au particles.^{16–17} Particles were assembled into close-packed monolayers on solid substrates by several methods.^{18–22} A close-packed layer of polystyrene particles (1 μ m diameter) was fabricated using the capillary attractive force, and the optical properties of this particle array were studied.²³

Patterning of particle layers was realized by several methods.^{26–49} Micropatterns of randomly deposited particles were fabricated by gas jet^{26,27} or ink jet^{28,29} printing methods. Whitesides et al.³⁰ used electrostatic interactions to direct the patterning of gold disks having a 10 μ m diameter on functionalized surfaces. The micropattern of gold disks was successfully fabricated by environmentally friendly processes such as the solution process at room temperature. This technique does not need special devices and conditions and can be applied to not only planar

substrate but also curved substrate such as a fiber. Hammond et al.³¹ fabricated micropatterns of SiO₂ particles (710 nm diameter) or latex particles (530 nm diameter, 1 μ m diameter) on a patterned polyelectrolyte multilayer in solution at room temperature using electrostatic interactions. They demonstrated control over the density and selectivity of particle adsorption using a polyelectrolyte multilayer platform and adjustment of three conditions: pH of the colloid suspension, ionic strength of the suspension, and concentration of added surfactant. Micropatterns of particles that have chemical bonds to substrates were achieved by several techniques. We fabricated two-dimensional particle arrays in solution through the formation of siloxane (Si–O–Si) or ester bonds (–COO–) at room temperature.³² Yoon et al.³³ modified the surface of zeolite and a glass substrate with several functional groups. Micropatterns of zeolite were fabricated on the glass substrates in solution by various covalent linkages. These techniques extended the variety of patterning methods and introduced strong adhesion in particle assembly.

Two-dimensional patterns with steady repeatability in the particle array were also achieved by techniques such as the probe technique,^{34–35} electrophotography method,^{36–38} a micromold method and gravity,³⁹ a micromold and a lateral capillary force,⁴⁰ and a patterned Au film and drying process of colloidal solution.⁴¹ In addition, patterns with high arrangement accuracy have been realized by several techniques. Selective immobilization of single particles into predetermined positions with respect to adjacent particles was realized by nanolithography. We demonstrated precise arrangement of SiO₂ particles (500 nm diameter) at desired positions by nanolithography using an AFM probe.³² Mirkin et al.⁴² arranged polystyrene latex particles (190 nm diameter, 930 nm diameter, 1 μ m diameter) on MHA (16-mercaptohexadecanoic acid) dots deposited by holding the atomic force microscopy (AFM) probe. These techniques can realize precise arrangement of nano-/microparticles. Kim et al.⁴³ fabricated micropatterns of the fcc (or hexagonal close packed (hcp)) structure from polymer particles (200 nm diameter) using a micromold. We recently reported a novel process to produce a pattern of close-packed particle monolayers and several kinds of particle wires.³² A self-assembled monolayer (SAM) of octadecyltrichlorosilane (OTS) was modified to adopt a pattern of silanol groups and octadecyl groups. The patterned SAMs were then immersed into the solution containing SiO₂ particles. Particles were arranged selectively on regions of silanol groups in the solution, and thus, micropatterns and wires of particles were fabricated. Miyazaki et al.^{44,45} fabricated photonic crystals such as two-dimensional close-packed structure⁴⁴ and fcc (or hcp) structure⁴⁵ from latex particles (0.6–2 μ m diameter) by the micromanipulation technique in a scanning electron microscope. Although this can be applied to produce novel particle structures, the technique requires hours for the arrangement. Xia et al.⁴⁶ brilliantly fabricated large colloidal crystals with their (100) planes of fcc structure oriented parallel to the substrate, which

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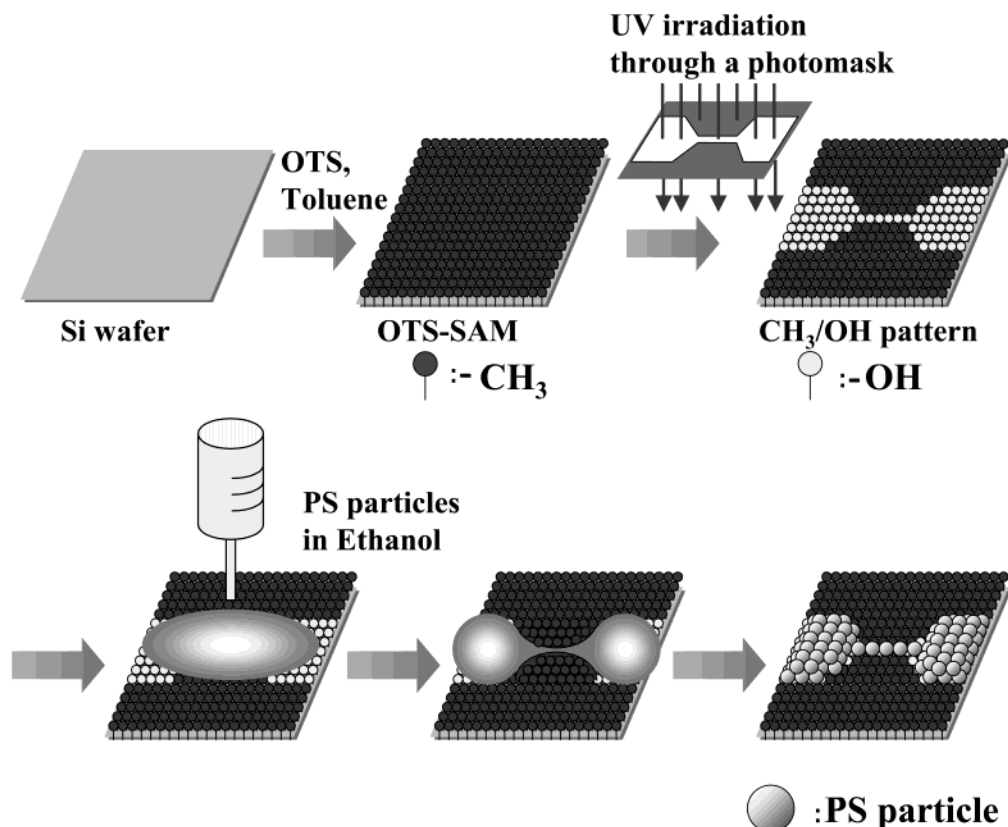


Figure 1. Conceptual process for fabrication of a particle wire using a patterned SAM and a liquid bridge.

has a two-dimensional regular array of square pyramidal pits. 3D opaline lattices having such orientation over areas as large as several square centimeters were constructed from polystyrene particle (250 nm diameter, 480 nm diameter, 1.0 μm diameter) in the solution through self-assembly. This technique does not need special devices such as electron beam writing in the assembling process, and the silicon templates should be robust enough to be used many times. Ozin et al.⁴⁷ described two processes, microfluidic colloid crystal self-assembly and spin-coating colloid crystal self-assembly, for particle assembly on silicon wafers. Patterns of V-shaped grooves inside a Si(100) were prepared by chemical etching to be used as templates for microfluidic assembly. A drop of an aqueous dispersion of SiO_2 particles (840 nm diameter) was added at the interface between the patterned silicon wafer and the flat block to fabricate the patterns of fcc colloid crystal parallel lines. Additionally, a particle suspension was spread on the wafer having an array of square-pyramid-shaped etch pits by spin coating. (100)-oriented colloid crystals having fcc structure were formed in etched pits within 2 h. Colloid crystals were fabricated rapidly within lithographic patterned silicon grooves by these self-assembly processes under moderate conditions.

Here, we developed a novel process for two-dimensional self-assembly of spherical particles using a liquid mold and its drying process. We fabricated particle wires that have high accuracy of arrangement at room temperature on hydrophilic regions of a patterned SAM. Particles were assembled to have regularity in their array by capillary force in the drying process. Patterns of a close-packed particle layer and particle wires were fabricated in the solution previously.³² Severe control of many factors was necessary to realize a close-packed structure and high accuracy because capillary force cannot be used in the solution. A close-packed structure can be easily obtained in our unique process compared with our previous

process.³² Additionally, assembly of particles was obtained in hydrophilic regions that were covered with solution-containing particles and was not obtained in hydrophobic regions that were not covered with solution. Liquid mold determined the positions for particle assembly resulting in high site selectivity for patterning compared with the patterning in the solution.³²

Experiment

OTS SAM was prepared by immersing the Si substrate in an anhydrous toluene solution containing 1% vol OTS for 5 min under an N_2 atmosphere.^{50–54} OTS SAM was modified to create two silanol regions (3 mm \times 3 mm) and a line (10 μm) of silanol groups between them by UV irradiation (184.9 nm) for 2 h through a photomask (Figure 1). The UV-irradiated regions became hydrophilic due to the formation of Si–OH groups, while the nonirradiated part remained unchanged; i.e., it was composed of hydrophobic octadecyl groups, which gave rise to patterned OTS SAM. To confirm successful film formation and functional group change, water drop contact angles were measured for irradiated and nonirradiated surfaces. Initially deposited OTS SAM had a water contact angle of 96°, while the UV-irradiated SAM surface was saturated (contact angle < 5°). This observation indicated successful fabrication of SAM patterned with octadecyl/silanol groups (Figure 1). Polystyrene particles in water (150 μL) (550 nm diameter particle or 820 nm diameter carboxylated particle, 10 wt %, dispersed in water, Seradyn Co., Ltd.) were further dispersed in ethanol (3 mL) or water (3 mL) and poured onto a patterned OTS SAM. The contact angles of the ethanol

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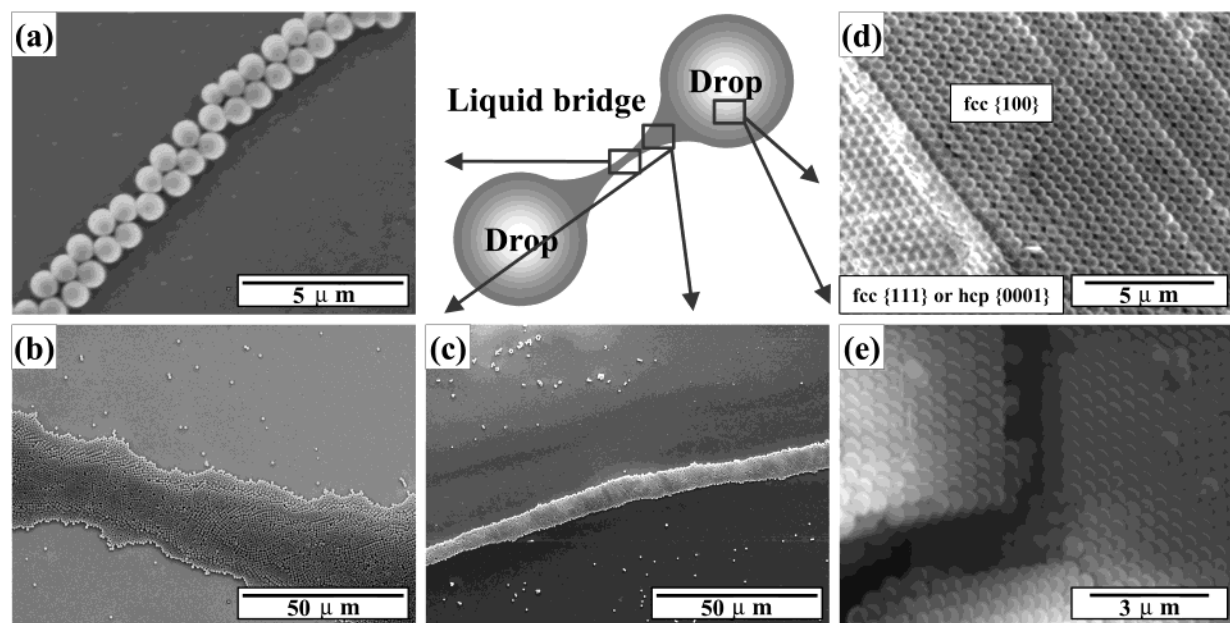


Figure 2. SEM micrographs of particle structures fabricated from aqueous solution containing microparticles using a liquid bridge: (a–c) particle wires constructed from a triangular lattice (close-packed structure); (d, e) a close-packed 3D structure.

solution or water solution measured $10\text{--}20^\circ$ or 96° on the OTS SAM, respectively, while they were saturated (contact angle $<5^\circ$) on silanol groups. The droplets were observed to separate into two drops, and a bridge of solution was formed on a silanol line. The droplets and the liquid bridge were used as a mold for fabrication of a two-dimensional pattern of colloid crystals. After evaporation of the solution, substrates were observed by a scanning electron microscope (SEM, S-3000N, Hitachi, Ltd.).

The dispersibility of particles in the solution is very important for particle assembly, and high dispersibility is necessary to form a close-packed structure. The zeta potentials of particles dispersed in the solutions were examined by direct measurement of electrophoretic mobility using an electrophoretic light scattering spectrometer (Zetasizer 3000HS, Malvern Instruments Co., Ltd.). The zeta potentials of polystyrene particles (550 nm diameter) in water, carboxylated particles (820 nm diameter) in water, polystyrene particles in ethanol, and carboxylated particles in ethanol were determined to be -38.3 , -50.2 , -53.9 , and -44.0 mV, respectively. Surface modification by carboxyl groups decreased the negative zeta potential in both solutions. Furthermore, particles in the ethanol had slightly low negative zeta potentials compared to those in water; i.e., the particles were slightly well-dispersed compared to those in water.

Results and Discussion

Polystyrene particles in water were poured onto a patterned OTS SAM and observed after evaporation of the water. The water at the liquid bridge evaporated in about 24 h to form a particle wire, and droplets at the two ends completely evaporated in about 48 h. In this manner, particle wires constructed from a close-packed structure, i.e., triangular lattice, were produced from the water solution (Figure 2a). The middle of a particle wire was narrower than its end (Figure 2b,c). The width of the particle wire does not depend on the width of the silanol line but rather on the interfacial tensions between solution and substrate, solution and atmosphere, and atmosphere and substrate. The silanol line was not used to decide the width of the particle wire but rather the position of the liquid bridge and particle wire. Close-packed structures were also formed on large silanol regions (Figure 2d,e). The right-hand area of Figure 2d can be regarded as the $\{100\}$ plane of the fcc structure and the left-hand area can be regarded as the $\{111\}$ plane of the fcc structure or

the $\{0001\}$ plane of the hcp structure. The close-packed structure was thus considered to be an fcc structure.

Figure 3 shows particle wires and 3D structures fabricated from ethanol solution containing polystyrene particles. The ethanol at the liquid bridge evaporated in about 1 min to form a particle wire, and droplets at the two ends evaporated in about 20 min. The liquid bridge of ethanol evaporated faster than that of water for several reasons. The saturated vapor pressure of ethanol (59 mmHg (0.078 atm) at 25°C) is higher than that of water (24 mmHg (0.031 atm) at 25°C), explaining the difference in the evaporation rate of the two droplets. The ratio in evaporation rate of the ethanol liquid bridge to the ethanol droplets is higher than that of the water liquid bridge to the water droplets. This can be explained as follows: Water has high surface tension (71.8×10^{-3} N/m at 25°C) compared with ethanol (22.0×10^{-3} N/m at 25°C). Ethanol existed along patterned hydrophilic regions with small meniscus at the angle between droplets and a liquid bridge. However, water formed large meniscus at the angle between droplets and a liquid bridge, causing a wide line width of water liquid bridge compared with ethanol on our patterned surfaces. Additionally, the water liquid bridge was higher than that of ethanol due to high surface tension. These made the cross-section area of water larger than that of ethanol. The thick liquid bridge evaporated slowly because of its large volume and low vapor pressure calculated from the Kelvin equation in which the smaller convex liquid surface gives rise to higher internal pressure and faster evaporation rate.⁵⁵ Furthermore, the solution at the droplets flowed into a liquid bridge, and this further complicated the evaporation mechanism.

A narrow particle wire was formed at the center of the liquid bridge (Figure 3a,b), and wide wires were formed at the edges of the liquid bridge (Figure 3c) along the silanol line. The particle wire in Figure 3a is not a close-packed structure and is constructed from a square lattice, which is a metastable phase compared with a close-packed structure. High dispersibility of particles is necessary to form a close-packed structure in the solution. However,

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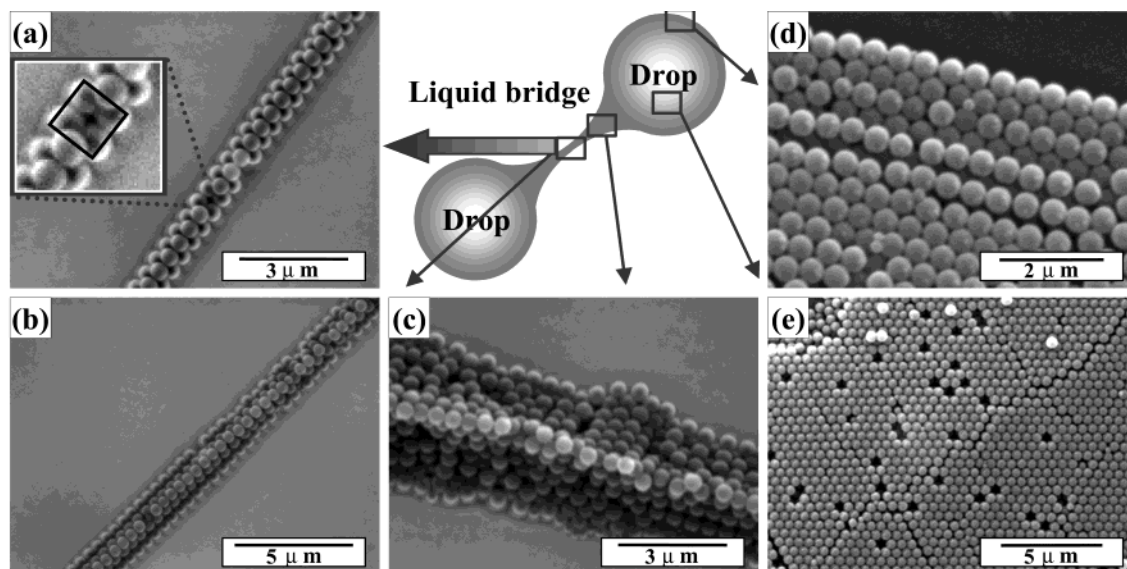


Figure 3. SEM micrographs of particle structures fabricated from ethanol solution containing microparticles using a liquid bridge: (a, b) particle wires constructed from square lattice; (c) particles deposited on edge of silanol line; (d, e) close-packed 3D structures.

the particles dispersed well in ethanol, and the dispersibility of particles in ethanol is similar to that in water. This shows that the non-close-packed structure was caused not only by the influence of dispersibility but also by many other factors. Movement and rearrangement of deposited particles are necessary to construct a close-packed structure. However, the ethanol evaporated quickly and suppressed the movement of particles by liquid bridge force. Additionally, adhesion between particles and a substrate and cohesion between particles probably caused moderate suppression of the rearrangement of particles. Factors such as evaporation rate, interaction force between particles, and interaction force between particles and a substrate were important in the packing process. Close-packed 3D structures were also formed on large silanol regions (Figure 3d,e), and they contained many defects (Figure 3e). The ethanol evaporated so quickly that the particles did not rearrange well to form a close-packed structure during evaporation of ethanol. This is one of the factors of forming a loosely packed structure. To directly evaluate the effect of the evaporation rate, a similar experiment using ethanol was conducted in a small airtight container with small pinholes to allow the ethanol to evaporate slowly. The size and number of pinholes were adjusted for ethanol at the liquid bridge to evaporate in about 24 h. The particle wire constructed from a close-packed structure was formed after about 24 h, and droplets at both ends were dried after about 48 h. The close-packed 3D structures were formed in large silanol regions. The number of defects was smaller than that formed from the ethanol solution with a shorter time and was similar to that formed from water. The humidity in the container was close to 100%, and the saturated vapor pressure of ethanol was 59 mmHg (0.078 atm) at 25 °C. This showed that particles dispersed well in ethanol and the interaction between particles and a substrate was sufficiently weak to produce a close-packed structure in the drying process of 24 h. Additionally, the results showed that not only the interaction force between particles and that between particles and a substrate but also the evaporation rate needs to be controlled to fabricate particle wires.

Accuracy of particle arrangement was evaluated from Figure 3a as calculated in recent work.³² The center position $((x_i, y_i) \mu\text{m})$ of each particle in an upper layer was plotted to estimate the standard deviation. The bottom left corner of Figure 3a was set to be the origin of the x - y coordinate.

The approximated straight line $f(x)$ and its slope (θ) are represented as follows

$$f(x) = 1.3965x - 5.3344 \quad (1)$$

$$\cos \theta = 0.5822 \quad (2)$$

Standard deviation from the approximated straight line is described by the expression

$$S(\text{standard deviation}) = \frac{[\sum_i \{\cos \theta(f(x_i) - y_i)\}^2]^{1/2}}{n - 1} \quad (3)$$

where n is the number of particles ($n = 19$). The accuracy of the particle arrangement in Figure 3a was estimated to be $S = 1.63 \times 10^{-3}$. This is lower than that of the particle arrangement obtained in our previous work.³²

Conclusions

We developed a novel process to fabricate particle wires on hydrophilic regions of a patterned SAM. Ethanol or water containing particles were separated into two droplets with a liquid bridge between the droplets along hydrophilic regions of a patterned SAM. Particle wires constructed from a close-packed structure or non-close-packed structure were then formed through self-assembly between two droplets after drying of the solution.

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