

Amphiphilic silver particles for conductive inks with controlled wetting behavior



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HIGHLIGHTS

- Synthesis of amphiphilic silver particles.
- Surface modification of silver particles by amidation.
- Dispersion, contact angle, surface tension of silver inks.
- Aerosol jet printing of silver inks on polyimide.
- Conductivity by thermal and photonic annealing.

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ABSTRACT

Silver inks find applications in printed electronics as conductive electrodes. Amphiphilic silver microparticles are prepared by modifying PAA-capped particles with functional amines via an amidation reaction. These modified silver particles can be dispersed in a wide variety of solvents ranging from water ($\epsilon = 80.4$) to lipophilic alcohols ($\epsilon = 3-17$) to yield conductive inks with tunable wettability. Using these inks, we have demonstrated aerosol jet printing of conductive silver patterns (36 μm wide, 1.2 μm thick) on Kapton. Electrical resistivity of 3.7 $\mu\Omega\text{ cm}$ is obtained after thermal annealing at 225 $^{\circ}\text{C}$ for 5 min. Similar electrical resistivity (3.9 $\mu\Omega\text{ cm}$) is achieved after photonic annealing as short as 1 ms at 1.4 KV.

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1. Introduction

Conductive metallic inks are widely used in printed electronics, such as photovoltaics [1,2], displays [3,4], batteries [5,6], sensors [7,8], and biomedical devices [9,10]. Currently, silver is the most widely used conductive material for these applications representing over 90% of the materials used in a \$1.5B annual market. Hence, the ability to control the dispersion of silver particles and concomitantly formulate conductive inks with controlled surface tension, contact angle, and viscosity are critically important. Here, we demonstrate a facile route for synthesizing amphiphilic silver microparticles that can be readily dispersed in a wide range of solvents yielding inks with controlled wetting behavior.

Metal particles are typically synthesized in solution via reduction of metal precursors in the presence of surface capping agents and reducing agents [11–13]. Depending on the capping agent chemistry, the resulting particles are usually either hydrophilic [14,15] or lipophilic [16–18]. Recently, amphiphilic silver particles have been produced by using amphiphilic polymers [19–25] as capping agents during synthesis or by ligand exchange [18,20] after particle synthesis is completed. However, each of these approaches has inherent limitations. For example, amphiphilic polymer capping agents typically form micelles in solution that serve as tiny reactors limiting the overall particle size. Ligand exchange allows better control over particle size, but it is difficult to ensure stability of particles with tunable wettability.

Here, we report a facile synthesis route for creating amphiphilic silver microparticles using a simple amidation reaction [26–28]. We first create silver microparticles using water-soluble poly(acrylic acid) (PAA) as a capping agent. Next, we modify their surfaces by amidation reaction through a carboxy-amine coupling reaction

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(Fig. 1). This two-step synthetic procedure allows us to produce silver particles in water and then control their surface chemistries by the choice of the appropriate amine chemistries. There are three classes of amines of interest, (1) alkyl-terminated, (2) alcohol-terminated, and (3) hybrid-terminated amines (Table S1). We chose 3-morpholinopropylamine (MPA), which possesses an amine (NH_2) group, a propyl ($-\text{CH}_2-\text{CH}_2-\text{CH}_2-$) group, and a morpholino ($-\text{NC}_4\text{H}_8\text{O}$) terminal group, such that its hydrophilic–lipophilic balance (HLB) after amidation can become 7 (Table S2).

2. Experimental

Amphiphilic silver microparticles are synthesized by a modified process of our previous report [29,30], followed by surface modification by amidation reaction. In a typical procedure 8.4 g PAA (molecular weight = 5000 g mol^{-1} , 50 wt% aqueous solution) and 4.2 g PAA (molecular weight = $50,000 \text{ g mol}^{-1}$, 25 wt% aqueous solution) are dissolved in a mixed solution of 500 g water and 280 g diethanolamine (DEA) by stirring for 1 h at room temperature. While stirring vigorously, 140 g silver nitrate powder is added into this solution, followed by stirring for 30 min at room temperature. The resulting solution is then stirred at 80°C for 2 h. This step results in a mean particle size of 150 nm in diameter (Fig. 2). After cooling for 2 h, acetone (1200 ml), a poor solvent for the PAA capping agent, is added in order to induce particle precipitation. After decanting the supernatant, the coagulated particles are centrifuged at 5000 rpm for 30 min to further concentrate the particles. The concentrated particles are re-dispersed in 100 ml of water, sonicated for 1 h at room temperature, and precipitated again by adding 500 ml acetone. After decanting the supernatant, the precipitates are collected by centrifuging at 5000 rpm for 30 min (Fig. 1).

Surface modification of the PAA-capped silver microparticles is carried out by amidation reaction using functional amines. In a typical procedure, 25.4 g of the washed silver precipitates (89.1 wt% solids as silver, $\text{PAA}/\text{Ag} = 0.012$ by wt.) are dispersed in 50 ml *N*-

methylpyrrolidone (NMP) by sonicating for 3 h in water bath in the presence of 2.25 ml 3-morpholinopropylamine (MPA) and 2.38 ml *N,N'*-diisopropylcarbodiimide (DCI) as reaction activation agent (Fig. 1). The dispersion is then sonicated in a heated water bath at 65°C for 12 h, followed by particle collection by centrifugation at 9000 rpm for 6 h. The particles are re-dispersed in different solvents by sonicating for 30 min in a water bath at room temperature.

Aerosol jet printing is carried out on a polyimide (Kapton, CS Hyde Co.) and cover glass (VWR Cat. No. 48366-089) substrates using a printhead (Optomec) attached onto a 3-axis micro-positioning stage (ABG 10000 *x-y-z* motion stage, Aerotech Inc.), whose motion is controlled by computer-aided design software. A silver ink (27.5 wt% solids, 1:1 water:IPA by volume, 2.5 cP at 10 s^{-1}) is loaded in a glass vial and aerosols are formed using an ultrasonic atomizer at 45 V. The formed aerosols are translated onto substrates by a deposition nozzle ($\phi = 150 \mu\text{m}$, Optomec) using a N_2 -powered pressure controller. The sheath and core gas flow rates in the deposition nozzle depend upon ink rheology, nozzle diameter, and printing speed, but typically range from 10 to 100 sccm at $1\text{--}10 \text{ mm s}^{-1}$. Printing is performed under ambient conditions at a relative humidity of 40–50%.

Contact angle and surface tension of silver inks are measured by a goniometer (DSA100, Kruss). The silver particles and printed features are observed using a field emission scanning electron microscope (FESEM, Ultra55, Zeiss) after sputtering with Au/Pd for 30 s (EMS 300T D Sputter Coater). Printed silver features are annealed by a hotplate (HS40A, Torrey Pines Scientific) and photonic annealing system (Sinteron 2000, Xenon Corp.). Their electrical resistivity is measured using a four-point probe (RM3000, Jandel).

3. Results and discussion

Fig. 2 shows SEM images and size distributions of the silver microparticles before and after surface modification. Silver particles with mean particle size of 150 nm are obtained (Fig. 2a and b).

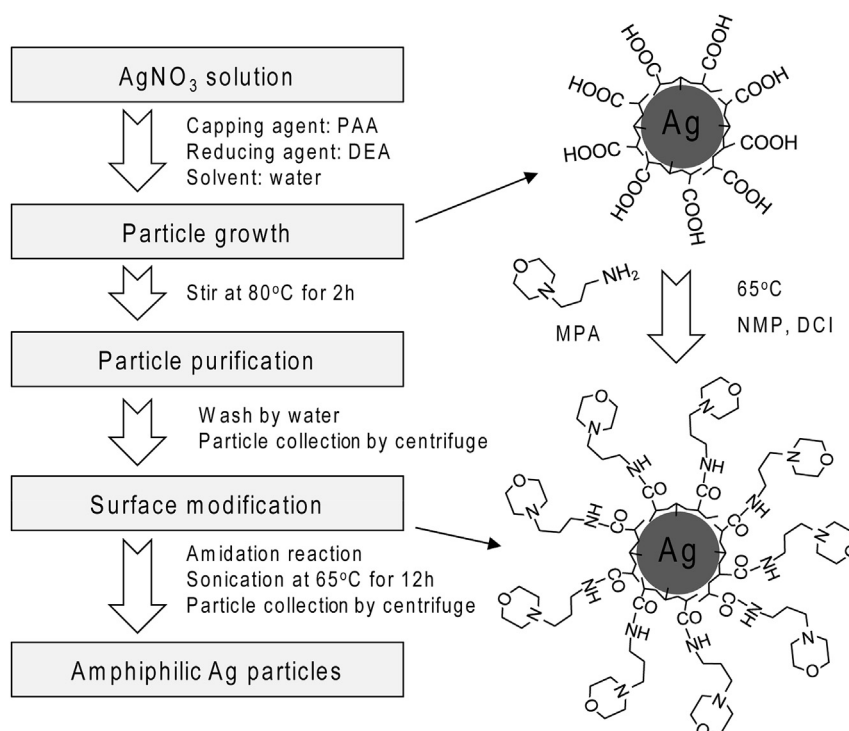


Fig. 1. Flow diagram and schematic illustration of PAA-capped Ag microparticle synthesis and surface modification by amidation reaction using MPA.

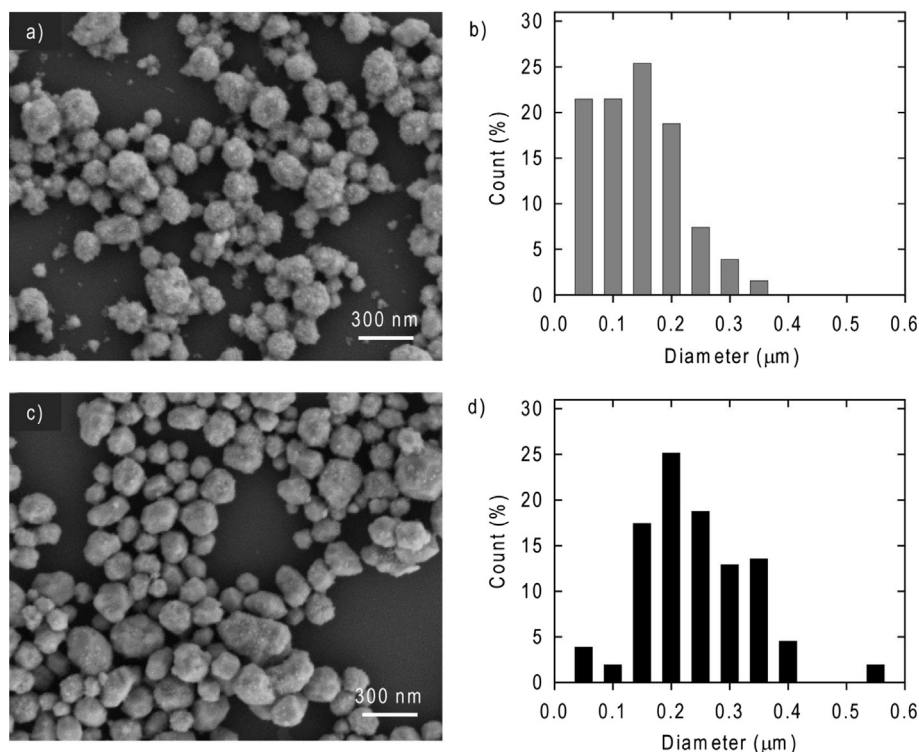


Fig. 2. SEM image (a) and size distribution (b) of hydrophilic silver microparticles produced in an aqueous AgNO_3 solution using diethanolamine as reducing agent and poly(acrylic acid) as capping agent. SEM image (c) and size distribution (d) of amphiphilic silver microparticles after amidation reaction using 3-morpholinopropylamine (MPA) at an initial $[\text{NH}_2]/[\text{COOH}]$ of 1.0.

After surface modification, the amphiphilic silver microparticles with a mean particle size of 200 nm are obtained (Fig. 2b and c). This modest size increase likely arises due to two reasons. Firstly, particle ripening occurs because amidation reaction performed long time (12 h) at elevated temperature (65 °C). Secondly, amidation forms amphiphilic particles, resulting in difficulties in particle collecting by centrifugation because they form stable dispersion in most of common solvents. We observed up to 1 wt% loss of small particles. This behavior can be seen clearly in the SEM images.

Fig. 3 shows dispersion of silver microparticles in different solvents before and after surface modification. The PAA-capped silver microparticles are well dispersed in solvents with high dielectric constant (ϵ), such as water, ethylene glycol, and NMP. However, these particles are unstable in alcohols with a broad range of dielectric constants (Fig. 3a). Amphiphilic silver microparticles synthesized using an initial $[\text{NH}_2]/[\text{COOH}]$ ratio of 0.1 exhibit improved dispersion in alcohols, yet significant flocculation is observed (Fig. 3b). By contrast, silver particles synthesized using an even higher initial $[\text{NH}_2]/[\text{COOH}]$ ratio of 1.0 could be readily dispersed in solvents (Fig. 3c) ranging from water ($\epsilon = 80.4$) to lipophilic alcohols ($\epsilon = 3\text{--}17$). Further tuning of their dispersion behavior is possible using different amines for the amidation reaction (Table S2 and Fig. S2).

Fig. 4 shows surface tension and contact angle of the amphiphilic silver microparticles dispersed in different solvents. The chemical and physical properties of solvents used in this study are provided in Table S3. The surface tension of the pure solvents ranges from 22 mN m^{-1} to approximately 72 mN m^{-1} . Upon adding 6 wt% amphiphilic silver microparticles synthesized with an initial $[\text{NH}_2]/[\text{COOH}]$ of 1.0, the measured surface tension values decrease by approximately 50% for each solvent investigated (Fig. 4a). We note that their surface tension values of 10–30 mN m^{-1} are within

the desired range for inkjet and aerosol jet printing of conductive inks [31–36]. Fig. 4b shows the measured contact angles of inks composed of 6 wt% amphiphilic silver microparticles suspended in varying solvents on both glass and Kapton. The lowest and highest contact angles observed ranged from 0 to 50° for inks formulated with IPA and water, respectively. Slight increases (~5%) of ink viscosity are observed after dispersing 6 wt% of silver particles in different solvents but they are basically governed by the inherent viscosity of solvent used (Fig. S3).

To demonstrate their printing behavior, we prepared a concentrated amphiphilic silver ink (27.5 wt% silver, in 1:1 water:IPA by vol.). This ink is aerosol jet-printed on Kapton at printing speed of 10 mm s^{-1} using a 150 μm nozzle (Fig. 5a). The patterned electrodes are 36 μm wide and 1.2 μm thick after printing and drying (Fig. 5b). Silver inks before amidation showed inhomogeneous wetting on polyimide and poor adhesion. In contrast, those after amidation exhibited good wetting on polyimide, resulting in uniform features with enhanced adhesion. Annealed films (~120 nm thick) showed no peel-off by the scotch tape test. Their electrical resistivities decrease with increasing annealing temperature and time. At a minimum annealing time of 5 min, we measured an electrical resistivity of 5800, 31.4, and 3.7 $\mu\Omega \text{ cm}$ at annealing temperatures of 175, 200, and 225 °C, respectively (Fig. 6b). SEM images highlight their electrode microstructures after annealing under these same conditions (Fig. 6a). The amount of polymer coated on silver particles is measured by thermogravimetric analysis (Fig. S1). Polymer/Ag mass ratios before and after amidation reaction are measured as 0.012 and 0.022, respectively. Polymer starts decomposing at 150 °C and degrades more quickly above 200 °C up to 400 °C. This decomposition behavior exhibits good agreement with the electrical resistivity data upon annealing.

High throughput, roll-to-roll printing [37] of flexible electronics requires even faster annealing times, such as those obtained by

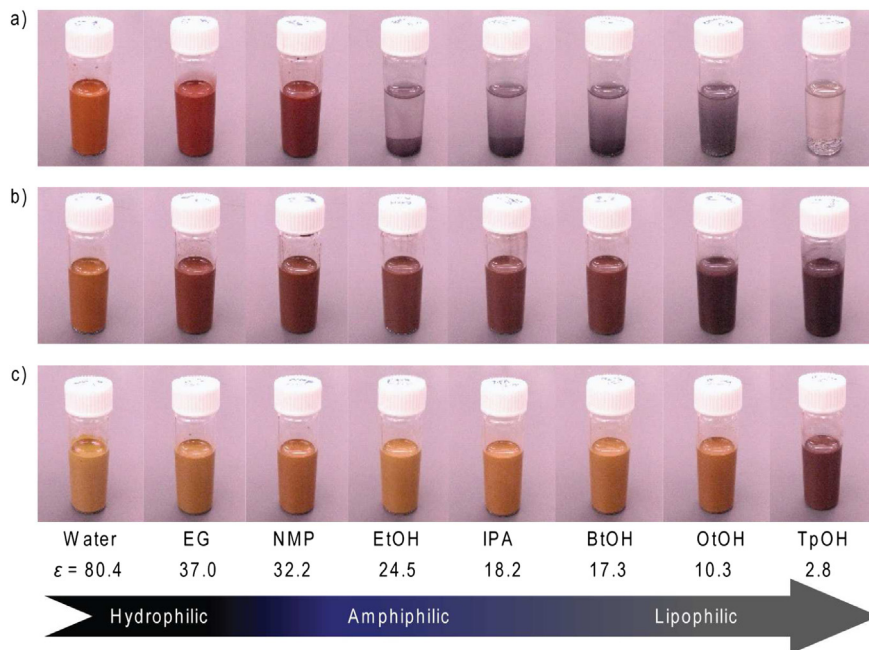


Fig. 3. Optical images of Ag microparticle inks (6 wt%) in different solvents. (a) PAA-capped Ag microparticles before amidation and (b–c) amphiphilic Ag microparticles after amidation using initial ratios $[NH_2]/[COOH]$ of 0.1 and 1.0, respectively.

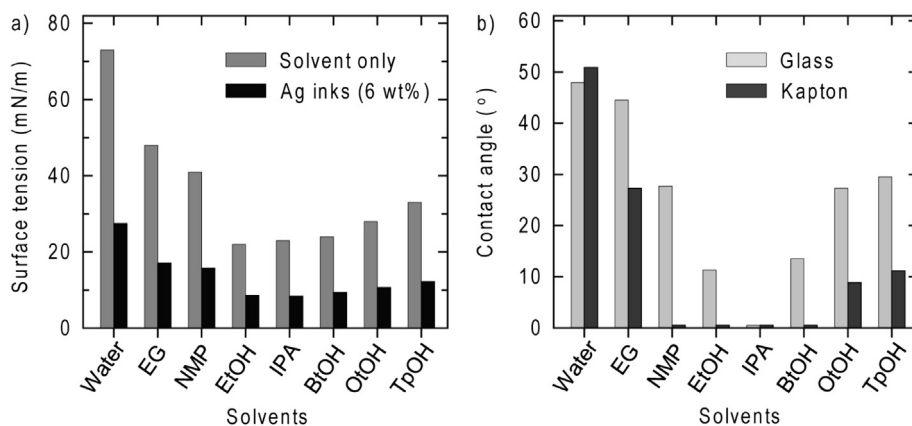


Fig. 4. (a) Surface tension of the amphiphilic Ag microparticle inks in different solvents. (b) Contact angle of the amphiphilic Ag microparticle inks on glass and Kapton of varying solvents.

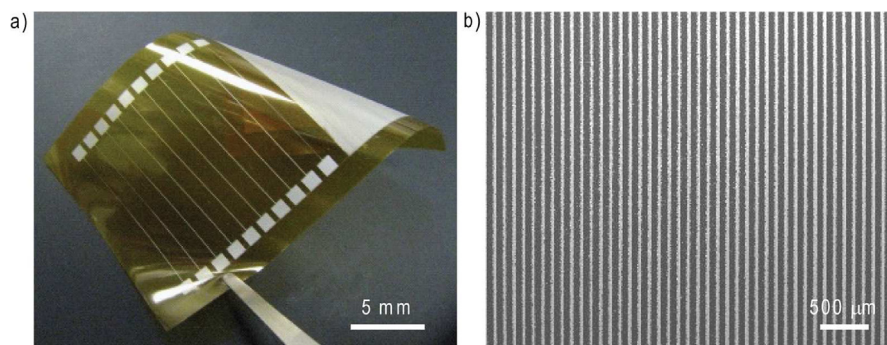


Fig. 5. (a) Optical image of the aerosol jet-printed Ag features on Kapton using a representative amphiphilic Ag microparticle ink with 27.5 wt% solids. (b) SEM image of the Ag line patterns shown in the top-right part of the optical image.

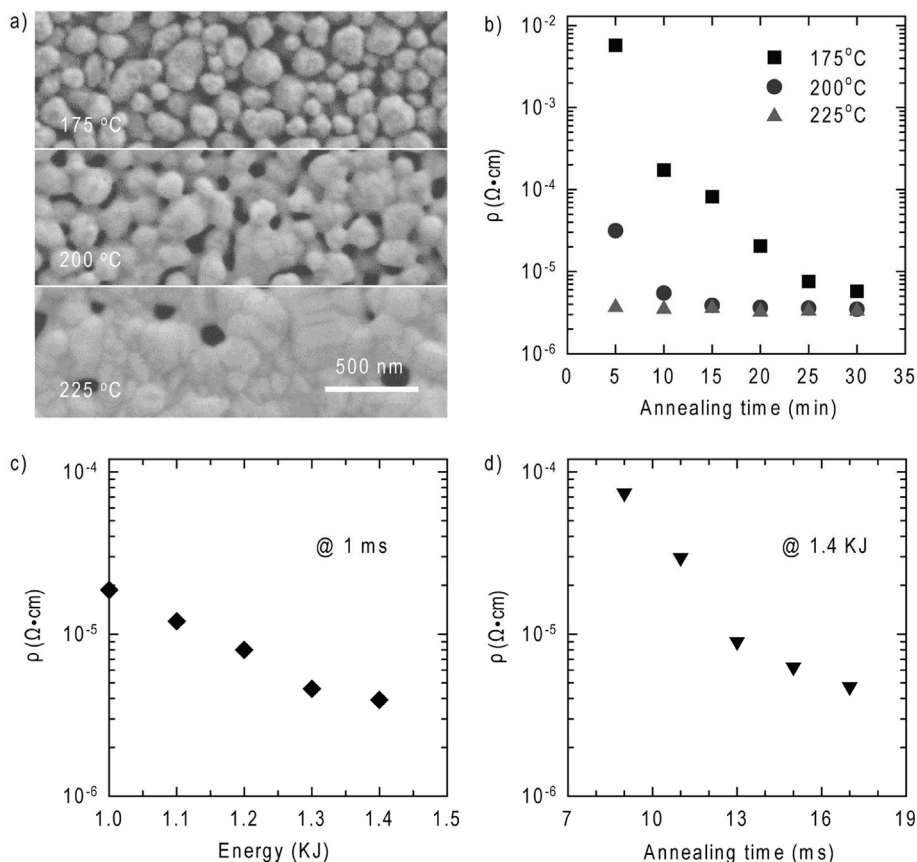


Fig. 6. SEM images (a) and electrical resistivity (b) of the Ag films annealed at different temperatures of varying annealing time. (c) Electrical resistivity for Ag films on Kapton after photonic annealing of varying the applied energy to the lamp. (d) Electrical resistivity of the Ag films on glass after photonic annealing as a function of annealing time.

photonic annealing using a high intensity pulsed xenon lamp that provides a broadband spectrum (0.24–1 μm). The silver films deposited by a 6 wt% ink in ethanol on Kapton exhibit the electrical resistivity as low as 3.9 $\mu\Omega\text{ cm}$ after photonic annealing for 1 ms at 1.4 KV (Fig. 6c). By contrast, silver films deposited on glass require a longer annealing time of ~ 17 ms to achieve similar electrical resistivity (Fig. 6d). Such differences arise due to the difference of light absorption properties of the two substrates used.

4. Conclusions

We have demonstrated a facile method for synthesizing amphiphilic silver microparticles via surface modification of PAA-capped silver particles by an amidation reaction. These modified particles can be readily dispersed in a broad range of solvents providing an effective way to control with wetting behavior of inks used in printed electronics. Using these amphiphilic silver inks, we have demonstrated the aerosol jet printing of conductive silver features on flexible plastic and glass substrates.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.matchemphys.2014.08.035>.

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