



Size Effects of Silver Nanoparticles on the Photovoltaic Performance of Dye Sensitized Solar Cells

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Authors' contributions

This work was carried out in collaboration between all authors. Author MYO designed the study. Author ED undertook the experimental work, performed the statistical analysis, wrote the protocol, wrote the first draft of the manuscript and managed literature searches. Authors SGA, HOA and EJ managed the analyses of the study and literature searches. All authors read and approved the final manuscript.

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ABSTRACT

The size effects of silver (Ag) nanoparticles (NPs) on the performance of a dye sensitized solar cells (DSSCs) through successive ion layer adsorption and reaction (SILAR) was investigated. A series of AgNPs with different SILAR cycles were synthesized on fluorine tin oxide (FTO) glass slides. The size effects of AgNPs on the photovoltaic (PV) performance of the formed DSSCs were investigated systematically. The performance, especially the photocurrent, and open circuit voltage of DSSCs containing AgNPs was significantly affected by the particle size of Ag NPs. The PV performance decreased with increasing size of AgNPs from one SILAR cycle to three SILAR cycles, the best performance was achieved using the anodes prepared with one SILAR cycle. The best cell shows a conversion efficiency (η) of 0.00910%. The cell exhibited a 36% improvement over the performance (0.00669%) of bare FTO-based device. The related PV performance enhancement mechanism and surface-plasmon resonances in DSSCs with Ag nanostructures are discussed.

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1. INTRODUCTION

The dye-sensitized solar cell (DSSC) is a device for the conversion of visible light into electricity, based on the sensitization of wide bandgap semiconductors. The performance of the cell mainly depends on a dye used as sensitizer. The absorption spectrum of the dye and the anchorage of the dye to the surface of TiO_2 are important parameters determining the efficiency of the cell. However, DSSCs emerged as a new class of low cost energy conversion devices with simple manufacturing procedures, environmentally friendly, and the light-weight thin-film structures are compatible with automated manufacturing [1]. Dye-sensitized solar cells suffer from durability problems that result from their use of organic liquid electrolytes containing the iodide/tri-iodide redox couple, which causes serious problems such as electrode corrosion and electrolyte leakage. Consequently, it adversely affects long-term performance and durability. The efficiency of DSSC system can be increased by incorporating metal nanoparticles NPs that can provide plasmonic enhancement. In surface plasmon resonance, the collective oscillation of free electrons confined at the surface of the metals can be induced when the frequency of incident light matches the plasmon frequency of irradiated metals. These collective charge oscillations result in substantially enhanced electric fields near the surface of NPs, which can facilitate both light absorption and charge separation.

The first experiments on Plasmon enhanced photovoltaics were in fact performed on organic and dye solar cells. As early as 1991 Hayashi et al. [2] observed an improved efficiency of an organic solar cell when propagating surface plasmons were excited in a metal contact of the cell. The influence of a *localized* Plasmon excitation in metal clusters on performance of an organic solar cell was reported by Stenzel et al. [3]. In their experiments, Cu metal clusters outperformed Ag and Au particles. The enhancement was attributed to the intensified near-field around the particles. Recently, many efforts have been devoted to increasing the light harvesting efficiency by introducing plasmonic structures into various solar cells. Tzu-ming et al. observed a 45% enhancement in the power conversion efficiency over a broad wavelength

range with the inclusion of plasmonic gold nanoparticles (NPs) [4]. Won yeop rho et al. fabricated a dye sensitized solar cells with Ag nanoparticle (NP)-embedded TiO_2 nanotube arrays by using UV irradiation. The energy conversion efficiency was increased from 4.64 to 6.14% by the Ag functionalization, a 32% enhancement, which is attributed to the surface Plasmon resonances present along the entire length of the TiO_2 nanotube arrays [5]. Furthermore, the AgNPs more effectively enhanced the energy conversion efficiencies in front-illuminated DSSCs than in back-illuminated ones. Derkacs et al. [6] reported that an engineered enhancement in short-circuit current density and energy conversion efficiency in amorphous silicon solar cells is achieved via improved transmission of electromagnetic radiation arising from forward scattering by surface plasmonpolariton modes in Au-nanoparticles deposited above the amorphous silicon film. The addition of AgNPs into the active layer significantly enhances carrier mobility but decreases the total extracted carrier which lead to improved photovoltaic parameters [7]. Bartosz et al. [8], reported an improved performance in photovoltaic polymer solar cells by increasing the amount of Ag in TiO_2 (by 3, 5, 7, and 10%). Higher PV performance was received by introducing TiO_2 with 5% of Ag. Also Iwan et al. [9] investigated the influence of amount of silver in a hole transporting layer on the performance of a bulk heterojunction polymer solar cells. They obtained a power conversion efficiency (PCE) of 2.16% under 100 mW cm^{-2} light intensity with $60 \mu\text{L}$ of Ag-NPs. But along with the increase amount of Ag-NPs from 60 to $150 \mu\text{L}$, the PCE decrease was found.

In this study, AgNPs with different SILAR cycles were synthesized on porous TiO_2 films fabricated on fluorine-doped SnO_2 (FTO) substrates. The size effects of AgNPs on the PV performance of the formed DSSCs were investigated systematically. The performance characteristics of the plasmonic DSSCs were analysed. An overall conversion efficiency of 0.00910% was obtained when the size of AgNPs was around 16 nm, which had a 36% improvement over the performance (0.00669%) of bare FTO based device. The related PV performance enhancement mechanisms and surface-plasmon resonances in DSSCs with Ag nanostructures are analysed and discussed.

2. EXPERIMENTAL SECTION

2.1 Synthesis of Nanocomposite Material for Profiling

We used dip coating method to synthesize the Ag nanocomposite on the glass substrate. The microscope slide was cleaned with laury sulphate and then rinsed with water 3 times. Thereafter dipped into a beaker containing a mixture of 40 mmoles concentrated tetraoxosulphate (iv) acid (H_2SO_4) and 40 mmoles chromic acid to make the surface hydrophilic for 10 min, the sample was thereafter rinsed with water. After making it hydrophilic, it was immersed in 2 moles $SnCl_2$ for 2 min then rinsed with distilled water for 2 min, then immersed at 0.35 moles silver nitrate ($AgNO_3$) for 2 min and rinsed with mixture of 150ml distilled water (H_2O) and 0.4 moles hydrochloric acid (HCl) for 15 sec. This procedure is called one cycle; the number of cycles was varied upto 3 cycles to obtain the thickness of the silver deposited.

2.2 Fabrication Process

The FTO electrodes were washed with laury sulphate then later rinsed with water six times in an ultrasonication bath for 10 min then finally washed in propanol. The photoanode was prepared by first depositing a blocking layer on the FTO glass, followed by the nanocrystalline TiO_2 . The blocking layer was deposited from a 2.5 wt% TiO_2 precursor and was applied to the FTO glass substrate by spin coating and subsequently sintered at $500^\circ C$ for 45 min. The 9 μm thick nanocrystalline TiO_2 layer was deposited by screen printing. It was then sintered in air for 30 mins at $500^\circ C$. The silver was deposited on the bare surface of the TiO_2 with different cycle through successive ion layer adsorption and reaction (SILAR). We used the SILAR because it allows us to control the thickness of the film by varying the number of cycles. We spin coat $TiCl_4$ (40 mmoles) at 2000 rpm and thereafter anneal at $300^\circ C$ to $350^\circ C$ for 30 min. To ensure the silver is protected, we treated it with 40 mmoles solution of $TiCl_4$ prepared at $40^\circ C$, then raise the temperature to $70^\circ C$ and finally annealed at $300^\circ C$ to $350^\circ C$. SiO_2 was deposited on the Ag using SILAR method with sodium silicate ($Na_2O(SiO_3)$) as the precursor. The minimum number of cycles that gave the cells stability was five cycles. The first cell with one Ag cycle had five cycles of SiO_2 , the second cell with two Ag cycles had ten cycles of SiO_2 and the third cell with three Ag cycles had fifteen cycles of SiO_2 .

The counter electrode was prepared by screen printing a platinum catalyst gel coating onto the FTO glass. It was then dried at $100^\circ C$ and fired at $450^\circ C$ for 30 min. The method of heating in water (Aq.) was used to extract the dye. Distilled water was the solvent for aqueous extraction. 5 g of the sample was measured using the analytical scale (OHAUS Corporation-USA) and dipped in 50 ml of the solvent heated to $100^\circ C$ for 30 min after which solid residues were filtered out to obtain clear dye solutions. Roselle extract is rich in anthocyanins. It was reported that anthocyanin obtained from roselle are delphinidin and cyanidin complexes [10,11]. The chemical structure of cyanidin and delphinidin in the hibiscus sabdariffa dye is shown in Fig. 4a.

The sintered photo anode with different SILAR cycles were sensitized by immersion in the sensitizer solution at room temperature overnight. Sensitization was achieved by immersing the photoanode in the extracts. The cells were assembled by pressing the photoanode against the platinum-coated counter electrode slightly offset to each other to enable electrical connection to the conductive side of the electrodes (Fig. 1). Between the electrodes, a 50 μm space was retained using two layers of a thermostat hot melt sealing foil. Sealing was done by keeping the structure in a hot-pressed at $100^\circ C$ for 1 min. the liquid electrolyte constituted by 50 mmoles of iodide/tri-iodide in acetonitrile was introduced by injection into the cell gap through a channel previously fabricated at opposite sides of the hot melt adhesive, the channel was then sealed.

2.3 Characterization

The current-voltage ($I-V$) data was obtained using a Keithley 2400 source meter under AM1.5 (100 mw/cm^2) illumination from a Newport A solar simulator. Scanning electron micrographs of the nanocrystalline TiO_2 films are taken with Carl Zeiss SEM. The absorption spectrum of the dye, spectra of various prepared AgNPs suspensions with and without dye were recorded on Ava-spec-2048 spectrophotometer. The cell active area was 1.8 cm^2 . Thickness measurement was obtained with a Dektac 150 surface profiler. Sheet resistance was obtained with a signatone four point probe resistivity apparatus.

3. RESULTS AND DISCUSSION

Fig. 1 shows the absorbance of the dye and various prepared AgNPs suspensions with and

without the dye within the wavelength range of 350-1000 nm along with the size growth of the Ag particle from 16 to 48 nm which correspond to the number of cycles. The absorption peak of hibiscus dye was observed around 550 nm (indicated in Fig. 1a), and the optical absorption enhancement was observed in the dye-loaded plasmonic nanocomposite films. The relative changes in optical absorption of the AgNPs suspension films are shown in Fig. 1b. The relatively broad and strong enhancement is observed in the range of 380–650 nm with a maximum enhancement around 550 nm, which coincides with the localized surface plasmon resonance (LSPR) band position of decorated AgNPs (Fig. 1c). This enhanced absorption and broadened spectrum absorption range of the photoanodes were mainly attributed to the SPR of AgNPs, which interacted with the dye, enhancing dye absorption that resulted in more charge carrier generation [12]. These features suggest that dye molecules in the vicinity of AgNPs can absorb more photons, presumably due to the intensified near-field effect of the surface plasmon and spectral overlap between the dye and surface plasmon, which may eventually lead to an increase in the number of charge carriers and J_{sc} values.

Fig. 2 shows SEM images of differently sized AgNPs deposited on the FTO surface using SILAR method.

The particle size is around 16 nm, 32 nm and 48 nm as shown in Figs. 2a, b and c, respectively. Fig. 3 shows the photocurrent density–voltage ($J - V$) curves of the DSSCs with varying silar cycles 0, 1, 2, 3 cycles. Based on the curves in Fig. 3, the *fill factor* (FF) and solar cell efficiency (η) were determined following the equations:

$$FF = \frac{P_{max}}{P_{in}} = \frac{J_{max} V_{max}}{J_{sc} V_{oc}} \quad (1)$$

$$\eta = \frac{FF \times J_{sc} \times V_{oc}}{P_{IRRADIANCE}} \cdot 100\% \quad (2)$$

Where V_{max} = maximum voltage (V); J_{max} = maximum current (mA/cm²); J_{sc} = short current (mA/cm²); V_{oc} = open circuit voltage (V) and $P_{IRRADIANCE}$ = light intensity (mW/cm²).

The open-circuit voltage (V_{oc}), short-circuit current density (J_{sc}), fill factor (FF), and overall conversion efficiency (η) are summarized in

Table 1. The performance of DSSCs fabricated with anodes deposited on bare FTO substrates was provided for comparison in the Table 1.

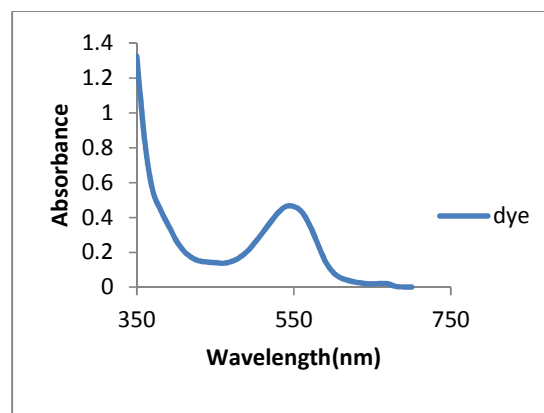


Fig. 1a. UV-Vis spectra of the dye

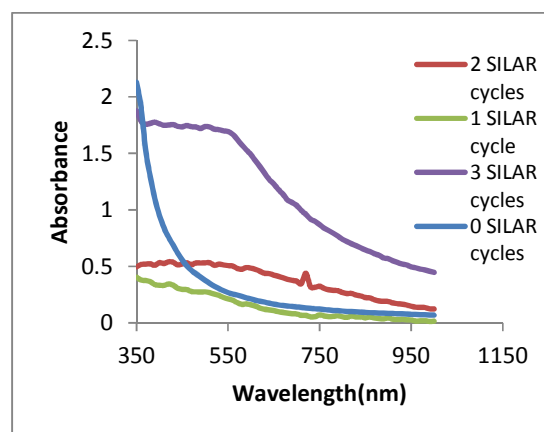


Fig. 1b. UV-Vis spectra of various prepared AgNPs suspensions without dye

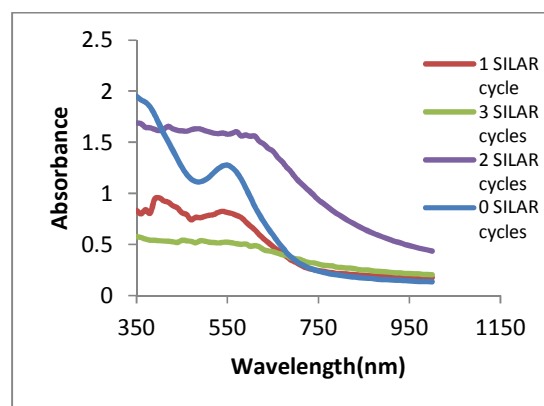


Fig. 1c. UV-Vis spectra of various prepared AgNPs suspensions with dye

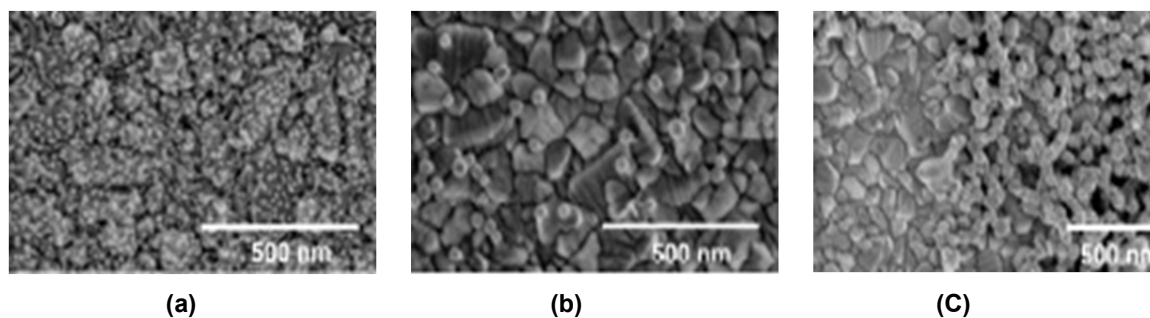


Fig. 2. SEM images of (a) one SILAR cycle, (b) two SILAR cycles and (c) three cycles

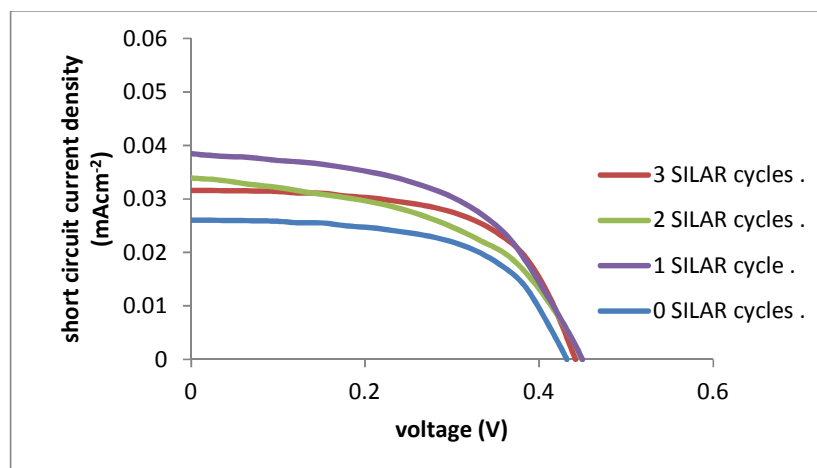


Fig. 3. The photocurrent density–voltage ($J - V$) curves with varying silar cycles

Table 1. Performance characteristics of DSCs fabricated with different anodes under 100 mWcm^{-2}

Sample	$J_{sc} (\text{mAcm}^{-2})$	$V_{oc} (\text{V})$	FF	$\eta (\%)$
FTO/TiO ₂	0.0259	0.432	0.594	0.00669
FTO/TiO ₂ /AgNPs(16 nm)	0.0385	0.450	0.526	0.00910
FTO/TiO ₂ /AgNPs(32 nm)	0.0339	0.449	0.488	0.00743
FTO/TiO ₂ /AgNPs(48 nm)	0.0316	0.442	0.507	0.00708

As can be seen from Table 1, the performance, especially the photocurrent, and open circuit voltage of DSSCs containing AgNPs was significantly affected by the particle size of AgNPs. The PV performance decreased with increasing size of AgNPs from one silar cycle to three silar cycles, from Table 1, the best performance was achieved using the anodes prepared with one silar cycle. The best cell shows a short-circuit current density (J_{sc}) of 0.0385 mAcm^{-2} , open-circuit voltage (V_{oc}) of 0.45 V and fill factor (FF) of 0.526%, yielding the highest efficiency (η) of 0.00910%. The cell exhibited a 36% improvement over the

performance (0.00669%) of bare FTO-based device. The efficiency enhancement in the presence of silver can be seen to arise chiefly from an increase in photocurrent density and V_{oc} values. The enhanced J_{sc} is related to the light harvesting capability of dye molecules by plasmon-enhanced excitation.

From Fig. 3, the overall conversion efficiency of the DSSC is improved when Ag particles are added. Compared with pure TiO₂ films, the mixed films containing Ag particles exhibit an increase in the power conversion efficiency from 6.12 to 36%. It was once reported that DSSCs based on

anodes containing Ag particles with 0.05 - 0.15 wt% content exhibit an increase in the power conversion efficiency from 11.6 to 34.6% [12]. Better results were obtained using our proposed method. As shown in Fig. 3 and Table 1, the overall conversion efficiency was remarkably improved when plasmonic nano structures were included, which was caused by the increase in J_{sc} . Compared with the reference cell employing nc-TiO₂ as the photoanode.

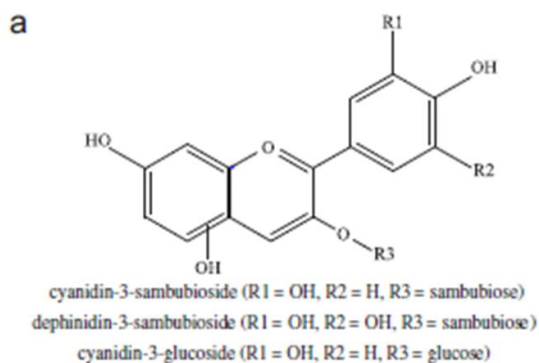


Fig. 4a. Chemical structures of: (a) cyanidin and delphinidin in rosella dye

As well known, silver has long been regarded as being catalytically active. However, AgNPs dispersed on metal-oxide supports are active catalysts for a variety of chemical reactions. It has been demonstrated that the unique catalytic activity strongly depends on the type of metal-oxide support, the preparation method, and particularly the size of the Ag clusters.

In our work, when AgNP was small, the catalytic effect of AgNPs sited on TiO₂ support could increase the reaction rate between the TiO₂/dye and the redox electrolyte in DSSCs, thereby reducing the corresponding electron transport resistance. Conversely, as the silver size became larger, AgNPs easily aggregated and formed islands as shown in Fig. 2, which could not preferentially attach to specific sites on the TiO₂ surface, resulting in the decrease of catalytic activity.

In the conventional DSSCs, the dyes absorb incident light and generate electrons in excited states, which inject into the TiO₂ NPs. The oxidized dye molecules are regenerated by electrons transferred from iodide. The regenerative cycle is completed by reducing triiodide to iodide at the counter electrode. The electrons in TiO₂ diffuse to the current collector (FTO). In the plasmon-enhanced DSSCs using

AgNPs, AgNPs were exposed to the electrolyte, resulting in slightly low V_{oc} which may imply that exposed AgNPs can act as recombination centres. In plasmonic solar cells, incorporated metal nanoparticles may have several roles: (i) to increase the light harvesting due to the strong near-field effects of LSPR; (ii) generation of hot electrons by surface plasmon excitation; (iii) to act as electron recombination sites, [13]. These factors can competitively have an impact on the device performance. The enhanced J_{sc} is related to the light harvesting capability of dye molecules by plasmon-enhanced excitation. Thus, the slight decrease in V_{oc} can be explained by the down-shifted Fermi level due to the plasmonic particles [14].

The J_{sc} and V_{oc} both decreased when the AgNPs content is above one SILAR cycle. The reason for this may be explained as follows: Not all of the AgNPs in photoanode were entirely coated by TiO₂ to form the mixed film. Therefore, some of the bare AgNPs in the AgTiO₂ network structure may be eroded by electrolyte and oxidized to Ag⁺ ions [15]. The latter act as a recombination center, reducing the number of charge carrier, thus resulting in a decrease in J_{sc} and V_{oc} . In addition, as the number of SILAR cycles increased the mixed films might result in blockage of sunlight which would prevent the incident light from reaching the TiO₂ NPs, resulting in the decrease in the photocurrent density. The combined effects of these factors resulted in the dependence of the performance of the plasmonic DSC on the Ag particle size. Hae-Jin Kim and Dae-Eun Kim once reported that the decrease in efficiency due to increasing surface roughness was found to be proportional to the light transmittance [16]. As a consequence, the recombination probability between electrons and holes may increase, so J_{sc} would decrease. In addition, higher concentrations of AgNPs may cluster to form larger AgNPs groups with lower electron storage capability, reducing V_{oc} [17].

4. CONCLUSIONS

A series of TiO₂ photoanodes with differing amounts of AgNPs were investigated. AgNPs with different sizes were grown on the TiO₂ deposited on the FTO through successive ion layer adsorption and reaction. The performance of the DSSC highly depended on the Ag particle size. The J_{sc} , V_{oc} and η decreased with increasing SILAR cycles. The results showed that adding AgNPs to TiO₂ photoanodes

significantly improved the performance of the DSSCs by increasing short-circuit current and open-circuit voltage. The best performing DSSC contained one SILAR cycle of AgNPs, The plasmonic DSSC based on hibiscus sabdariffa dye gave a short-circuit current density (J_{sc}) of 0.0385 mAcm^{-2} , open-circuit voltage (V_{oc}) of 0.45 V and fill factor (FF) of 0.526%, yielding the highest efficiency (η) of 0.00910%. The cell exhibited a 36% improvement over the performance (0.00669%) of bare FTO-based device lacking Ag. The increase of J_{sc} is attributed to the enhanced light absorption and broadened absorption spectral range of the composite photoanode due to the SPR of the AgNPs, while the V_{oc} increase may be reasonably related to the more negative quasi-Fermi energy of the AgTiO₂ composite system due to the enhanced electron capture and storage capability resulting from AgNPs doping.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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