



Development of promising surface enhanced Raman scattering substrate: Freckled SiO₂@Au nanocomposites



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ABSTRACT

This paper describes SiO₂@Au core-shell nanocomposites (NCs) as an excellent surface enhanced Raman scattering (SERS) substrate in this emerging field. The network of monodispersed silica (SiO₂) core of ~430 and 880 nm sizes with varying shell thickness from 12–50 nm was synthesized. The synthesized freckled SiO₂@Au NCs provide much better surface consistency and in tune generate a huge SERS signals enhancement. The study confirmed that the appropriate shell thickness and core size are responsible for the dramatic enhancement of the SERS signal intensities of the analyte crystal violet (CV) molecule by an order of 10¹²–10⁹. The SiO₂@Au core-shell NCs with 880 nm core and 30 nm shell thickness showed the maximum enhancement in SERS signals of order 10¹² using CV analyte molecule while the NCs with diameter 430 nm and 20 nm shell thickness produced the maximum enhancement of 10⁹ corresponding to 1620 and 1618 cm⁻¹ peaks respectively at the excitation wavelength of 532 nm. The advantage of choosing freckled SiO₂@Au core-shell NCs instead of nanoparticles (NPs) is that the core being dielectric provides additional electric field to Au nanoshell. Thus it generates more domains on the surface, is responsible for the enhancement of SERS signals and has been shown to be excellent substrate for SERS sensing applications. The results showed that the SiO₂@Au core-shell NCs with 880 nm core and 30 nm shell thickness act as an excellent substrate for SERS sensing.

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1. Introduction

The surface enhanced Raman scattering (SERS) is an advancement of Raman scattering which overcome some of the limitations of normal Raman scattering [1]. The SERS provides many fold enhancement in Raman signal intensity, which is sufficient for single molecule detection [2]. Due to its usefulness in various fields such as trace analysis, bio diagnosis, in vivo study, etc. the SERS has been receiving renewed interest in recent years [3,4]. It has become an important spectroscopic tool owing to its single molecule detection ability, capability of providing structural information for analytes of interest, minimal sample preparation and ease of operation [3,5]. However, there is lack of consistent techniques for controlling the properties of local fields at the metal surface which has been a major experimental limitation regarding quantification and understanding of SERS [3,6]. Thus, there is need for further development of sensitive SERS substrate that can be stored for a long period with possible promise of the enhancement of Raman signals.

The most commonly used SERS active substrates are Ag and Au colloids but the stability of colloidal solutions and reproducibility of aggregation are the two major problems. Although metal electrode substrates are more stable than colloids, they are less sensitive [7]. A new way to overcome these limitations is to produce a core-shell nano-scale material consisting of 'dielectric core' and 'metallic shell' which exhibits plasmon resonance that can be tuned from near UV to near IR [8]. Attracted by the unique optoelectronic and physicochemical properties, the gold nanoparticles (Au NPs) and core-shell gold nanocomposites (NCs) have widely been used which act as promising SERS substrate [9–11] where the tunability of the plasmon band in core-shell NCs has led to tremendous potential in chemical and biomedical fields [10].

The SERS activity depends not only on the nature of the metals but also on their shape [12], size [9,12,13] and thickness of shell and inter-particle coupling of NPs [12,14]. An ever-expanding technique in nanoscience has provided great opportunities to fabricate a wide variety of nanostructures with controllable size and shape [4,8,11]. Such concentric tunable geometry has been designed for more effective enhancement of Raman signals [6,8]. Accordingly, it is of great interest to extend the SERS substrate from inexact surfaces and disordered structures to well-defined and ordered nanostructures to gain the highest SERS activity [15]. Therefore, for the first time we have

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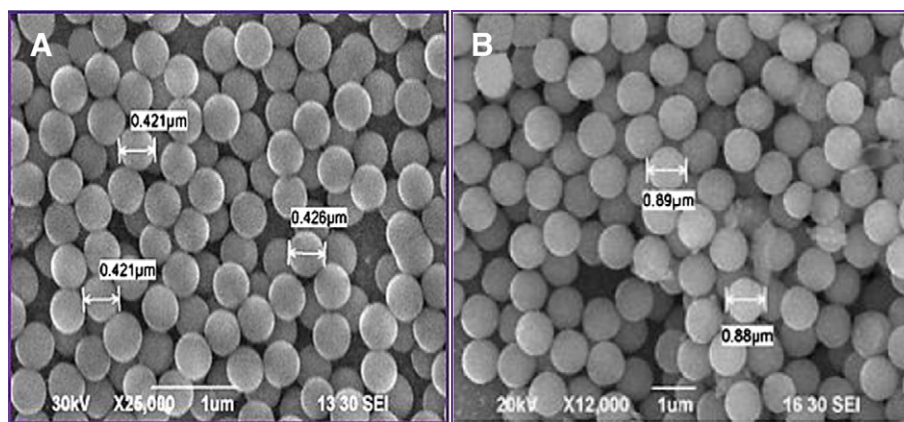


Fig. 1. (A) SEM image of SiO₂ nanoparticles ~430 nm and (B) SEM image of SiO₂ nanoparticles ~880 nm.

synthesized and report the dielectric cores of SiO₂ of two different sizes ~430 nm and 880 nm with varying shell thickness of Au NPs from 12–50 nm and shown to have significant enhancement of SERS signals, using CV as an analyte, due to application of a particular shell thickness. The present report illustrates an excellent enhancement of SERS signals which was achieved using freckled core–shell NCs with suitable thickness and definite core size.

2. Experimental

2.1. Chemicals and materials

Chloroauric acid (HAuCl₄·3H₂O), tetraethylorthosilicate (TEOS) and crystal violet (CV) were purchased from Sigma-Aldrich (USA) and used as such. Anhydrous ethanol (C₂H₅OH) and ammonium hydroxide (NH₄OH) were supplied by the Sinopharm Chemical Reagent Co. (China), while potassium carbonate (K₂CO₃), sodium borohydride (NaBH₄) and 3-mercaptopropyltrimethoxysilane (MPTMS) were procured from the Alfa Asser (China). Silicon wafers were supplied by the Xin Bai Ri Technology Co. (Beijing, China). All the chemicals used were of analytical grade and distilled millipore water was used throughout the experimentation.

2.2. Fabrication of silica NPs

Monodispersed silica nanoparticles were synthesized by Stöber procedure with minor modifications [16]. TEOS solution (0.1 mL) was used as silica source to obtain silica NPs. Two different size silica NPs were obtained by varying the amounts of C₂H₅OH and NH₄OH. The SiO₂ NPs

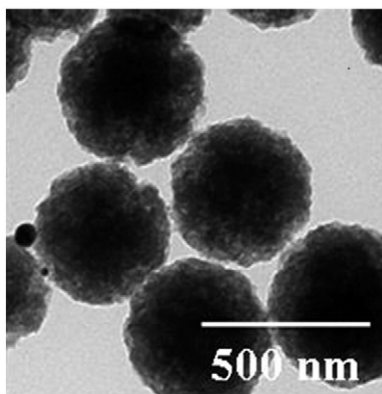


Fig. 2. TEM image of –SH group functionalized SiO₂ nanoparticles.

of 430 nm size were obtained with 15 mL of C₂H₅OH and 1 mL of NH₄OH while 880 nm sized SiO₂ NPs were obtained with 10 mL of C₂H₅OH and 2.5 mL of NH₄OH. SiO₂ NPs were functionalized with –SH group by heating the mixture of SiO₂ NPs and MPTMS (60 μL) in 2-propanol (30 mL) at 60 °C for 4 h. The –SH functionalized SiO₂ NPs were washed by ethanol five times through centrifugation and redispersed in water (20 mL) as a stock solution.

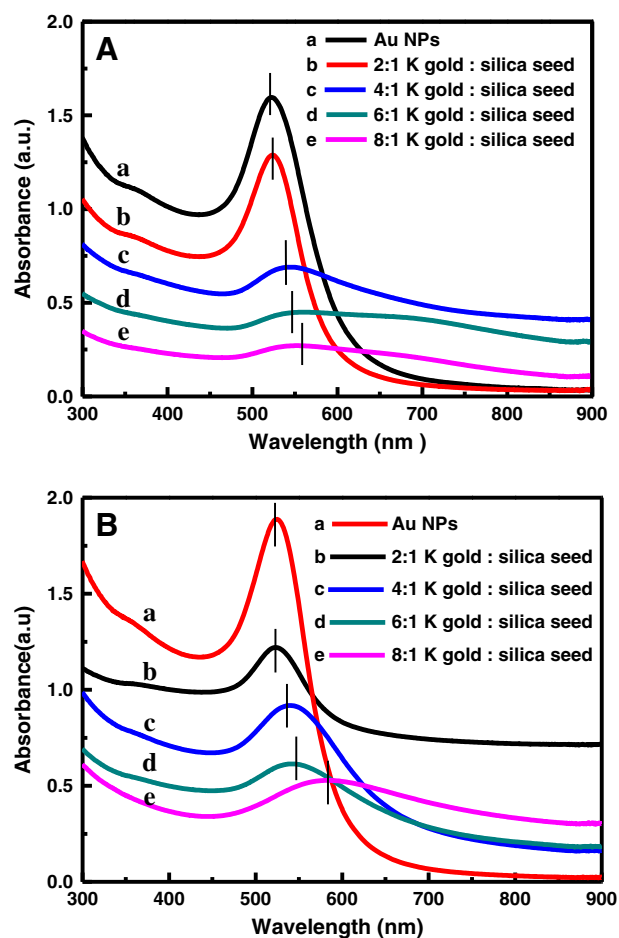


Fig. 3. (A&B). In both a is SPR peak of Au NPs while b, c, d and e are SPR peaks of freckled SiO₂@Au core–shell NCs with core size 430 and 880 nm in A and B respectively obtained on addition of 20, 40, 60, 80 mL gold hydroxide solution to 10 mL of Au–silica seed solution having 0.0053 mg silica in each 10 mL solution.

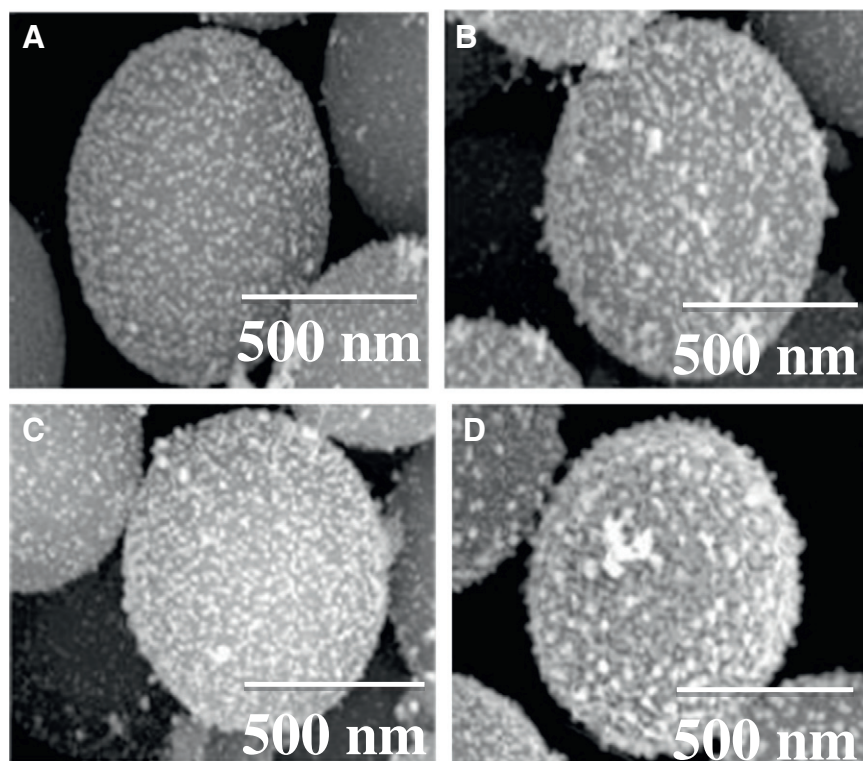


Fig. 4. FESEM images of the SiO_2 @Au NCs synthesized using ~ 880 nm SiO_2 particles with different gold hydroxide/Au-silica ratios and for different amounts of 0.053 mol of NaBH_4 solution (A) 50, 1.0 mL (B) 50, 1.6 mL, (C) 100, 1.6 mL and (D) 500, 1.6 mL.

2.3. Fabrication of freckled core-shell nanocomposites

SiO_2 @Au core-shell NCs were synthesized by our three step procedure reported elsewhere [11]. The first step involves the formation of gold seed with silica particles in which 1 mL functionalized silica particles in water was stirred with 20 mL (6.25 mM) of gold solution and 4.5 mL (0.1 M) of NaOH solution ($\text{pH} = 7.0$) at 75°C for 10 min. The resulting silica gold seed solution was centrifuged and washed with water and re-dispersed in 40 mL water. In the second step, 28 mg K_2CO_3 with 100 mL millipore water and 1.5 mL of 25 mM gold solution were stirred and aged in the dark for 12 h for the formation of gold hydroxide solution. Finally, gold hydroxide solution was mixed with silica gold seed solution and 5.3 mM NaBH_4 with constant stirring for 10 min and thus the desired freckled SiO_2 @Au NCs were obtained.

Two sets of SiO_2 cores (430 and 880 nm) were obtained by varying the amount of gold hydroxide solution into silica seed solution. Different sizes of core-shells were prepared by varying the thickness of Au NP shell over fixed sized SiO_2 core (430 nm) where the amount of gold hydroxide was varied from 20–80 mL. By the addition of 20, 40, 60 and 80 mL gold hydroxide solution to the silica seed solution; thicker gold shells of 6, 10, 15 and 25 nm were obtained. Thus different sizes of SiO_2 @Au NCs of 445, 450, 460 and 480 nm were obtained with 430 nm fixed core. Similarly, another set of core-shell NCs was synthesized with 880 nm fixed SiO_2 core where 895, 900, 910 and 930 nm size SiO_2 @Au core-shell NCs were obtained by the addition of 20, 40, 60 and 80 mL gold hydroxide solution.

3. Result and discussion

3.1. Characterization

Optical absorption spectra of Au NPs and SiO_2 @Au core-shell NCs were recorded on a 500 UV-VIS-NIR spectrophotometer Varian (USA)

and Hitachi 2010 (USA). Transmission Electron Microscopy (TEM) was used to investigate particle morphology. Field emission scanning electron microscopy (FESEM) images were recorded using a FEI/XL 30 (USA) equipped with energy dispersive X-ray (EDX) operated at 11 kV. The samples for FESEM study were prepared by depositing the Au NP and SiO_2 @Au NC solutions drop on silicon substrate followed by drying for ~ 10 h. Raman spectra were recorded with a Renishaw 2000 set up equipped with semiconductor laser (wavelength 532 nm). The laser power used in these experiments was ~ 0.2 mW while laser beam size was ~ 1.5 μm radii. Although the SERS spectra of Au NP and SiO_2 @Au NC solutions were achievable, they are not at all suitable for potential application as a sensor in molecular electronics and biomolecular recognition [17]. In the solutions, the movement of particles leads to the randomness of the hot spots that are responsible for SERS and thus affecting the quality of signal. However, the main emphasis was the collection of SERS spectra of CV using SiO_2 @Au. Thus, 20 μL of core-shell sample solutions with different sizes of core and shell were deposited on silicon substrate where 10^{-4} M solution of 5 μL CV was required for observing SERS spectra.

Fig. 1 (A & B) shows the SEM images of SiO_2 NPs while Fig. 2 shows the TEM image of -SH functionalized SiO_2 NPs. Fig. 1 (A & B) shows that the SiO_2 NPs are of ~ 430 and ~ 880 nm size and having smooth surfaces. Fig. 2 shows rough surface of the functionalized SiO_2 NPs where small gap of ~ 1.2 – 1.5 nm between different particles is clearly seen.

The plasmonic properties of these core-shell systems were initially characterized by a UV-VIS-NIR spectrophotometer. The surface plasmon resonance (SPR) peak of 430 core size is shown in Fig. 3(A). The red shifts in SPR bands were observed from 522–565 nm when the ratio of SiO_2 -Au seed solution: gold hydroxide solution increases from 1–8 mL. It has been continually demonstrated that with increasing thickness of shell, red shift in SPR band is observed [4,11]. This is because of the fact that the number density of adsorbed Au NPs on silica dielectric core is more and spacing between them becomes smaller. Fig. 3(B) shows SPR peaks corresponding to the ~ 880 nm core size of SiO_2 @Au NCs.

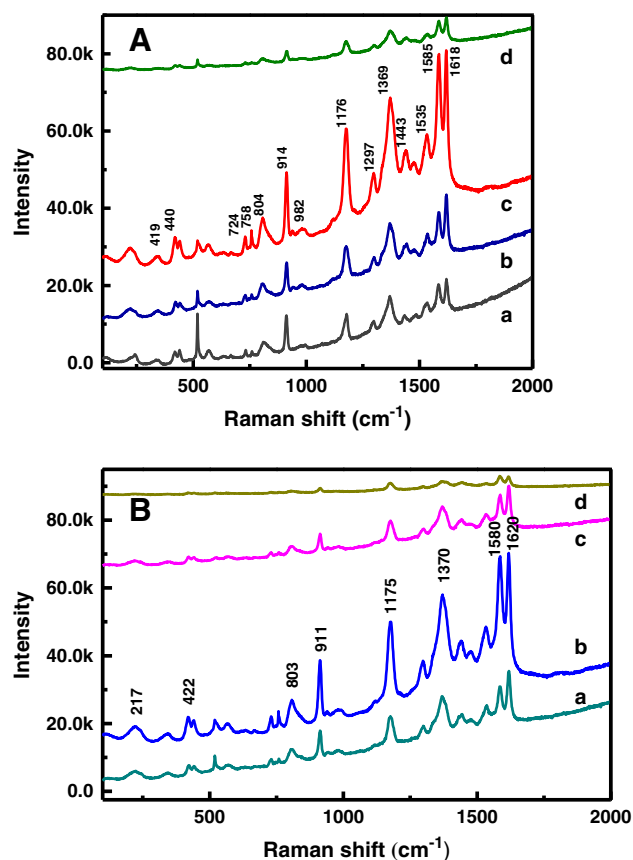


Fig. 5. A. SERS spectra of SiO₂@Au NCs with core size 880 nm and increased shell thickness (12, 20, 30 and 50 nm a to d respectively) using CV as an analyte molecule at 532 nm excitation wavelength. B. SERS spectra of SiO₂@Au NCs with core size 430 nm and increased shell thickness (12, 20, 30 and 50 nm a to d respectively) using CV as an analyte molecule at 532 nm excitation wavelength.

The shell thickness dependent SERS activity is well explained on the basis of the SPR. The width and red shift of the resonance peak for the freckled SiO₂@Au core-shell NCs increases due to plasmon hybridization [18]. Thus, the significant changes in the relative intensities of some of the vibrational bands in the SERS were observed first by varying the size of core and second by varying the thickness of the shell at 532 nm excitation wavelength. Fig. 4(A–D) represents FESEM images of SiO₂@Au NCs with core size ~880 nm while gradually increasing shell thickness from (A)–(D). The sizes 12, 20, 30 and 50 nm of the core-shell NCs were larger than SiO₂ particles accounting for a layer of ~6, 10, 15 and 25 nm Au NPs used in synthesizing SiO₂@Au core-shell NCs. The Au NPs of 27–30 nm size decorated on SiO₂ particles i.e. resulted SiO₂@Au NCs act as a promising SERS substrate. The FESEM images in Fig. 4 clearly show that the shells are not a continuous film of Au NPs and thus described as ‘freckled shell’.

3.2. Size and thickness dependent SERS activity of Au nanoshells

The SERS activity with altered shell thickness of SiO₂@Au NCs was assessed at first by using CV as an analyte molecule at 532 nm excitation wavelength and shown in Fig. 5A. It was observed that with increased shell thickness up to 30 nm, the SERS intensity also increased and decreased with further increase of shell thickness as shown in Fig. 5A(a to d). As shown in Fig. 5A(c), the maximum enhancement of the SERS signals occurs for SiO₂@Au NC spheres with a diameter of 880 nm and 30 nm shell thickness.

Reproducibility and SERS intensity is strongly dependent on the SERS substrate. Thus controllable thickness of Au shell and appropriate

core size has been introduced which characterizes outcomes in a high spatial density of the ‘hot spots’ with Raman enhancement as observed in the FESEM images (Fig. 4). These ‘hot spots’ caused the enhancement of the SERS signal intensity for molecules absorbed in the region between 400 and 1650 nm.

Raman spectra of CV (10⁻⁴ M) were recorded with SiO₂@Au core-shell NCs. The factors like surface structure, its coverage, complex enhancement mechanisms contribute in the enhancement of the SERS intensity [19,20]. The shells have not fully covered the SiO₂ core leaving some active sites as well as roughness which led to the enhancement of SERS signals [21]. However, at higher concentration no such active sites that were available caused the decrease in SERS signals intensity. The thickness of shell for SiO₂@Au is enormously less; less active site is accessible and so there is the least enhancement in SERS signal intensities as shown in Fig. 5A(a). The maximum enhancement in the SERS signal intensities with CV molecule was obtained for SiO₂@Au where the network of Au NPs on SiO₂ core is dense and is shown in Fig. 5A(c). As additional Au is deposited on to SiO₂ network, high intensity pores are no longer accessible and thus the Raman signal intensities decreased faster as shown in Fig. 5A(d).

As the peak intensity was observed to be optimum in spectrum {Fig. 5A(c)} so with the help of electromagnetic enhancement theory (EET), the enhancement factor (EF) was calculated for peaks observed in spectrum Fig. 5A(c) using following formula [17,18].

$$EF = \frac{I_{\text{SERS}}}{N_{\text{surf}}} \times \frac{N_{\text{bulk}}}{I_{\text{norm}}}$$

The value of N_{surf} i.e. the number of CV adsorbed on SiO₂@Au under this area was estimated to be 13 × 10⁹ molecules and the value of N_{bulk} i.e. the bulk sample of CV without SiO₂@Au was 17 × 10¹⁵ molecules. I_{SERS} and I_{norm} are the intensities of SERS and normal Raman peaks of a particular band respectively. The enhancement factors calculated by determining the number of core-shell on the surface for different peaks are shown in Table 1 where an excellent enhancement of the SERS signals up to 10¹² was achieved. The enrichment factors (EFs) calculated and shown in Table 1 are quite reproducible.

In order to properly understand the size effect of core on the SERS intensity, the SERS spectra of CV (10⁻⁴ M) with core size 430 nm with 12–50 nm thickness of shell was recorded and is shown in Fig. 5B. It has been observed from Fig. 5B that when core size is small, fewer Au NPs were anchored for optimizing the core-shell NCs. The maximum enhancement in the SERS signal intensities occurs for spheres with a diameter of 430 nm and 20 nm shell thickness and is clearly shown in Fig. 5B(c). By applying the same EET and EF formula, the maximum enhancement factor in this case was came out to be 10⁹ corresponding to 1620 cm⁻¹ at 532 nm [19].

4. Conclusion

The freckled SiO₂@Au core-shell NCs with adaptable size of core and different thickness of shell were synthesized. The FESEM images together with the Raman spectra showed that the thickness of the Au shell had substantial effect on enhancement of SERS signal intensities. The surface roughness along with the ‘hot spots’ due to nanogaps between the Au

Table 1

The enhancement factors for different peaks for CV adsorbed on SiO₂@Au NCs calculated using fixed the concentration of CV 10⁻⁴ M are quite reproducible.

| Peak (cm ⁻¹) | Assignment | EFs |
|--------------------------|-----------------------------|------------------|
| 1618(vs) | ν(C–C) stretching vibration | 10 ¹² |
| 1585(vs) | ν(C–C) stretching vibration | 10 ⁹ |
| 1369(s) | ν(C–N) stretching vibration | 10 ⁶ |
| 1176(vs) | ν(C–H) bending mode | 10 ⁴ |
| 914(s) | Ring skeleton vibration | 10 ³ |

NPs was responsible for the dramatic enhancement of the Raman signal intensities of CV molecule. The SERS results indicated that due to adaptable size of core and explicit thickness of shell freckled SiO₂@Au NCs act as an excellent Raman signal amplifier. The present study confirmed that the core size of 880 nm and shell of 30 nm produce an excellent enhancement factor of order 10¹² which acts as promising SERS substrate. This individual NC based SERS technique is simple, fast and inexpensive. Thus, the freckled SiO₂@Au core-shell NCs with particular nanoshells are ideal for enhancing the Raman signals.

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