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Gold nanoparticles supported on cellulose aerogel as a new efficient catalyst for epoxidation of styrene

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Abstract A new efficient heterogeneous catalyst was introduced for the epoxidation of styrene. The catalyst was obtained from deposition of gold nanoparticles on the cellulose aerogel. The catalyst was characterized with XRD, TGA, EDX, BET, FAAS and SEM. High yield and excellent selectivity were achieved for the epoxidation of styrene in solvent-free conditions at room temperature using H_2O_2 as a green oxidant during 1 h. The reaction has some advantages such as solvent-free and mild reaction conditions, low catalyst loading, high yield, excellent selectivity, green oxidant and short reaction duration. In addition, the catalyst is recyclable and applicable for six times without decrease in yield.

Keywords Cellulose aerogel · Epoxidation · Styrene oxide · Gold nanoparticles · Heterogeneous catalyst

Introduction

Aerogels are ultralightweight solid materials with an interconnected porous structure. The important characteristics of aerogels are large specific surface area, high porosity and low thermal conductivity [1–3]. Inorganic aerogels such as silica aerogels have some commercial applications in packaging, lightweight construction and structural insulation. The intrinsic fragility of inorganic aerogels is the drawback, which limits their practical applications where both high toughness and strength are needed. Organic aerogels based on cellulose are interesting due to their biological and sustainable origins [4]. Cellulose is a carbohydrate polymer made up of repeating β-*d*-glucopyranose units and consists of many hydroxyl groups giving the cellulose molecule a high degree of functionality. This most abundant natural biopolymer has the characteristic properties such as hydrophilicity, chirality, biodegradability and high functionality. Cellulose aerogels are generally less brittle, even flexible and easily compressed without disintegration [4].

Epoxidation of olefins is an important process in a number of important organic transformation reactions. Epoxides are industrially interesting compounds since they have applications in the synthesis of several perfume materials, anthelmintic preparations, epoxy resins, plasticizers, drugs and sweeteners [5]. One of the most interesting industrial epoxides is the styrene oxide. Styrene oxide can be used for producing epoxy resin diluting agent, flavoring agent, ultraviolet absorbent, etc., and is also an important intermediate in organic synthesis and pharmaceutical compounds synthesis such as Flouxetine and Norflouxetine [6]. Therefore, development of new routes for preparation of styrene oxide by an easier and a low-cost approach is of great interest to researchers working in this field.

Various styrene epoxidation approaches were reported, and for most of them hydrogen peroxide is an ideal oxidant from both environmental and economic viewpoints. Hydrogen peroxide is a relatively less expensive and environmentally safe and forms water as the only by-product. The epoxidation of styrene can be performed under strongly alkaline conditions with H_2O_2 as the oxidant [7]. However, the use of strong bases is highly undesirable due to the production of large amounts of industrial waste. Al_2O_3, MgO and CaO are efficient metal oxide for the epoxidation of styrene

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with hydrogen peroxide as the oxidant [7–9]. Recently, epoxidation of olefins with metals as the catalyst such as gold nanoparticles has attracted a great deal of attentions [10]. A series of S-containing organic–inorganic hybrid mesoporous silicas were used as supports for the fabrication of supported gold nanoparticle [11]. The catalyst showed high activity for epoxidation of styrene at 60 °C using H_2O_2. Gold nanoparticles supported on Y_2O_3 catalyzed the epoxidation reaction of styrene selectively at 75–97 °C [12]. Gold nanoparticles deposited on amine-functionalized nanoscale metal–organic framework MIL-101(Cr) was introduced as an efficient recyclable catalyst for epoxidation of styrene [13]. Numerous methods for the epoxidation of olefins with gold nanoparticles were reported [10].

Cellulose and its derivatives can be used as a support since they are renewable, biodegradable and non-toxic [14]. There are reports about cellulose derivatives as the support for some important catalysts such as Cu(0) [15], Pd(0) [16, 17], Cu(I)/Pd(0) [18] and Co(II) [19, 20]. In continuation of our efforts to develop new catalytic systems with cellulose as the support [17–20], herein a new efficient catalytic system was introduced for the oxidation of styrene by gold nanoparticles supported on cellulose aerogel (Au@CA) as a heterogeneous recoverable catalyst with H_2O_2 as a green oxidant in H_2O as a green solvent or solvent-free conditions where styrene oxide is obtained as the sole product. Cellulose aerogel was used as the support due to high porosity which can afford a high surface area for the gold NPs.

Experimental

Materials and methods

All reagents were purchased from Aldrich or Merck and used without further purification. Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) were performed with scanning electron microscope of TSCAN Company. X-ray powder diffraction (XRD) data were collected on an XD-3A diffractometer using Cu K_α radiation. Thermal gravimetric analysis (TGA) was performed with Linseis STA PT1000. Au(0) determination was carried out on an FAAS (Shimadzu model AA-680 atomic absorption spectrometer) with a hollow cathode lamp at 242.8 nm, using an air-acetylene flame.

Preparation of cellulose aerogel

A mixture of cellulose (4 g), urea (20 g), NaOH (3.8 g) and H_2O (180 mL) was sonicated for 10 min. Then, cellulose aerogel was obtained by freeze-drying the mixture for 12 h and washing with H_2O (3 × 10 mL).

Preparation of Au@CA

In a typical procedure, a mixture of H_3AuCl_4 (1 mmol) and cellulose aerogel (2 g) in 10 mL of H_2O was stirred at room temperature. After 24 h, a solution of $NaBH_4$ (2 mmol, 5 mL) was added to the mixture during 1 h and stirring continued for 24 h. Finally, the catalyst was separated via filtration, washed with H_2O (3 × 10 mL) and dried at 70 °C.

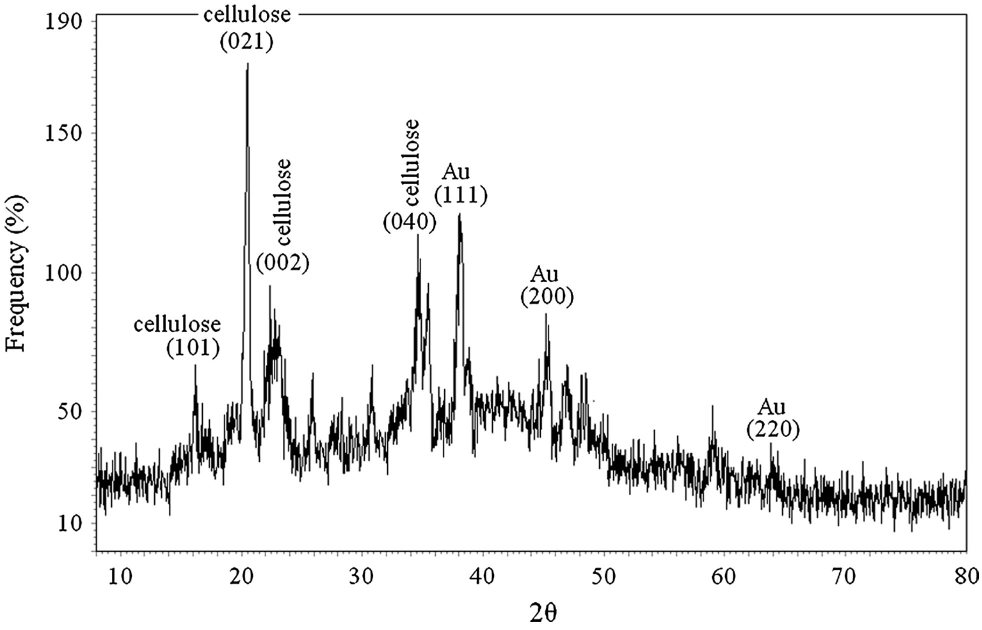

Fig. 1 XRD pattern of Au@CA

Typical procedure for the epoxidation of styrene

Styrene (0.10 g, 1.00 mmol) was added to a round-bottomed flask containing colloidal of Au@CA (0.04 g) in H_2O (5 mL). H_2O_2 (3 mmol) was added dropwise to the reaction vessel during 0.5 h. After 0.5 h, Au@CA was separated via filtration and washed with acetone (2 × 5 mL). The filtrate solvent was evaporated under vacuum and the product purified with column chromatography with *n*-hexane–ethylacetate (5:1).

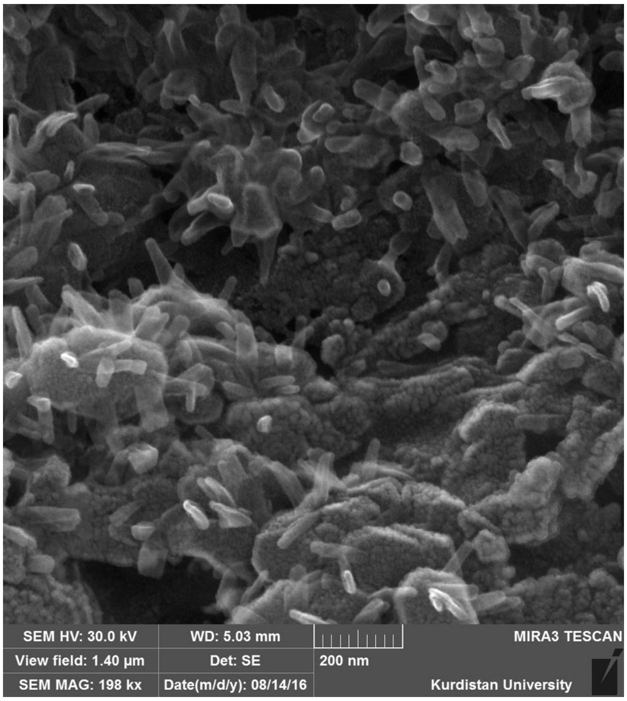

Fig. 2 SEM image of Au@CA

Results and discussion

For the preparation of the catalyst, H_3AuCl_4 was stirred with cellulose aerogel for 24 h, and then Au(I) was reduced to Au NPs with $NaBH_4$. The catalyst (Au@CA) was produced as a purple powder.

The catalyst was characterized with Brunauer–Emmett–Teller analysis (BET), X-ray diffraction pattern (XRD), flame atomic absorption spectroscopy (FAAS), SEM, energy-dispersive X-ray (EDX) and thermal gravimetric analysis (TGA). The specific surface area of the aerogel (S_{BET}), calculated from the BET equation, is about 192 m^2g^{-1}. The high surface area of cellulose aerogel can be assisted to perform the oxidation reaction with low catalyst loading.

The structure of Au@CA was analyzed by powder XRD with characteristic diffraction peaks of (111), (200) and (220) for gold NPs and (101), (021), (002) and (040) for cellulose aerogel (Fig. 1). These peaks confirmed the deposition of gold NPs on cellulose aerogel.

SEM image of the catalyst indicates deposition of rod-like gold NPs on the support with maximum average size

Fig. 3 EDX microanalysis of Au@CA

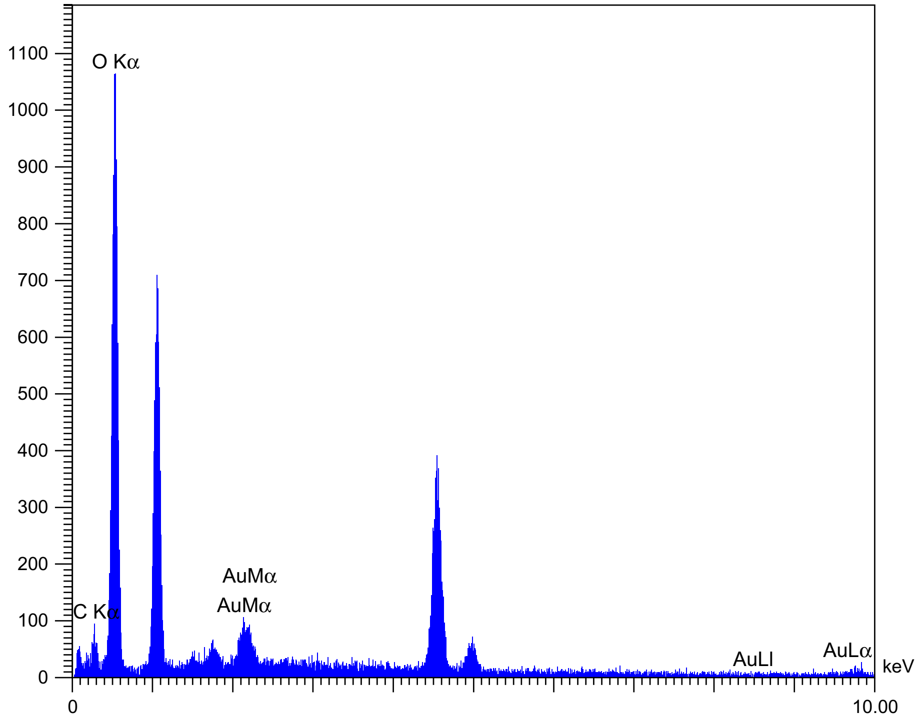

Fig. 4 TGA spectra of Au@CA

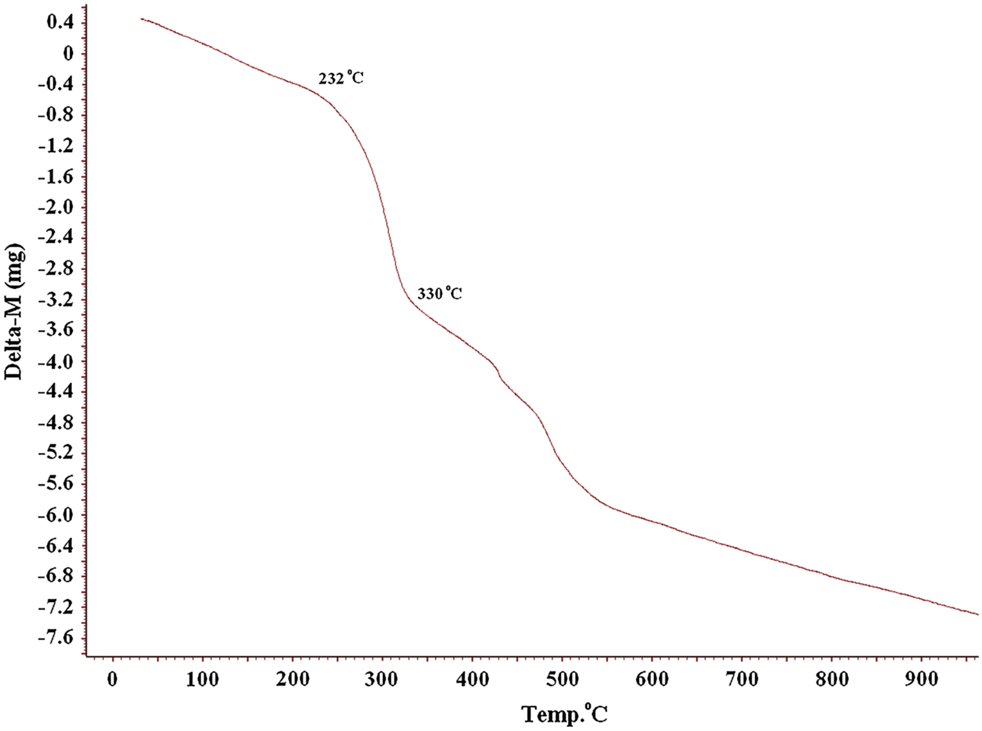

Table 1 Optimization of the reaction conditions for oxidation of styrene

Entry	Catalyst amount (Pd mol%)	Solvent	Time (min)	Product	Yield (%)[a]
1	0.13	H_2O	60	Styrene oxide	84
2	0.17	H_2O	60	Styrene oxide	96
3	0.21	H_2O	55	Styrene oxide	96
4	0.13	No solvent	60	Styrene oxide	87
5	0.17	No solvent	60	Styrene oxide	96
6	0.21	No solvent	60	Styrene oxide	96
7[b]	0.17	H_2O	60	Styrene oxide	83
8[b]	0.17	No solvent	60	Styrene oxide	91
9	0.17	EtOH–H_2O (1:1)	60	Styrene oxide	82
10	0.17	DMA	120	Styrene oxide	80
11	0.17	MeCN	120	Styrene oxide	81
12	0.17	EtOH	120	Styrene oxide	72
13	0.17	CH_2Cl_2	120	Styrene oxide	71
14	0.17	$PhCH_3$	120	Acetophenone	68
15	0.17	MeOH	120	Acetophenone	69

Reaction conditions: styrene (1 mmol), catalyst, H_2O_2 (3 mmol), solvent (5 mL)

[a] Isolated yield

[b] H_2O_2 (2 mmol)

between 81 and 89 nm (Fig. 2). The color of gold NPs depends on size and shapes of the NPs; for example, the nanorods of gold with size about 80 nm have purple color [21]. The purple color of Au@CA approved the size and shape of the gold NPs obtained from SEM.

The catalyst surface was analyzed with EDX microanalyses, which indicates the presence of Au (Fig. 3). The Au concentration obtained was 0.43 mmol Au per 1 g catalyst using FAAS analysis with calibration curve prepared with Au solution standards.

TGA of the catalyst showed that the catalyst has good thermal stability (dec > 232 °C) in air (Fig. 4). Another mass loss for the catalyst happened at 330 °C.

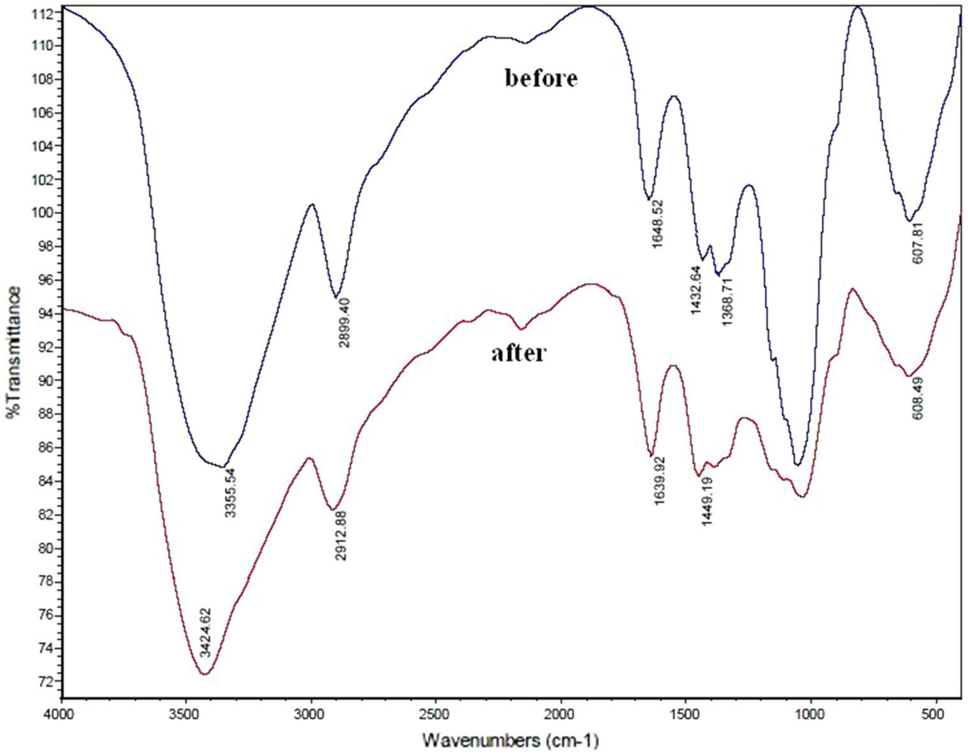

Fig. 5 FT-IR spectra for the catalyst before and after the reaction

The catalytic activity of Au@CA was evaluated in the oxidation of styrene. So, the oxidation of styrene (1) with H_2O_2 was investigated for the optimization of reaction conditions. It was found that 0.17 mol% Au (Table 1, entries 1–6) in H_2O or solvent-free conditions with three equivalents of H_2O_2 at room temperature are the best reaction conditions for the epoxidation of styrene. Oxidation of styrene proceeded to give styrene oxide (2) as the sole product with 96% yield in short reaction duration (1 h) without any by-product such as acetophenone or acetaldehyde. This is a controlled oxidation reaction of styrene since the formation of acetophenone or acetaldehyde is probable in oxidation of styrene. After screening a variety of solvents, H_2O and solvent-free conditions were determined to be the best conditions (Table 1, entries 9–15). The reaction needs 3 mmol H_2O_2 for obtaining high yields, and the yields decreased in low amounts of H_2O_2 in both H_2O and solvent-free conditions (Table 1, entries 7 and 8). The reaction in EtOH gave acetophenone as the by-product in 11% yield and determined with GC. For the reaction with toluene and methanol, acetophenone was obtained as the product, interestingly. Styrene oxide was obtained as the by-product of the reaction in toluene and methanol solvents with 4 and 21% GC yield, respectively. Room temperature is an important factor for this reaction, which gave more interest to the reaction.

Table 2 Successive trials by using recoverable Au@CA for epoxidation of styrene[a]

Trial	Recovered catalyst (g)	Yield (%)[b]
1	0.04	96
2	0.04	96
3	0.04	95
4	0.04	95
5	0.04	95
6	0.04	95

[a] Styrene (1 mmol), catalyst (0.04 g), H_2O_2 (3 mmol), H_2O (5 mL), r.t., 1 h

[b] Isolated yield

The reaction was examined using oxygen as an oxidant instead of H_2O_2. For this purpose, the reaction was performed with an oxygen balloon where 86% yield was obtained in long duration (24 h). In addition, the epoxidation reaction for cyclohexene and hexene did not perform in the optimized reaction conditions for styrene epoxidation.

Potential Au leaching into the reaction mixture was studied with FAAS analysis. For this purpose, sample was taken through a syringe filter during the oxidation reaction of styrene, the solvent was evaporated, and the residue was dissolved in HNO_3. The analysis of these samples with FAAS showed that the Au concentrations in the reaction solution were less than the detection limit. This result indicates that virtually no Au leached from the surface into the solution.

Table 3 Comparison of the results of Au@CA-catalyzed epoxidation of styrene with pervious reports

Entry	Catalytic system	Recyclable	Solvent	Time (h)	Temp. (°C)	Isolated yield (%) (I) or GC yield (%) (G)	Selectivity
1	Fe_3O_4-CuO@meso-SiO_2	Yes	CH_3CN	7.5	80	100 (G)	93
2	Au@silica	No	CH_3CN	14	80	98.5 (G)	82.8
3	Ag@Fe_3O_4	Yes	Toluene	0.25	Ref.	86.4 (G)	95.1
4	Au@CA	Yes	H_2O or solvent-free	1	r.t.	96 (I)	100

Also, we did not observe any change in IR spectrum for the catalyst recovered from the reaction (Fig. 5).

Recyclability of the Au@CA was examined in the epoxidation of styrene in H_2O. After carrying out the reaction, the catalyst was separated via filtration as a violet solid, washed with EtOH (2 × 5 mL) and reused. Only minor decreases in the reaction yield were observed after six repetitive cycles for this reaction (Table 2).

The results of our catalyst are compared with previous reports about epoxidation of styrene with respect to their recyclability, solvent, reaction duration, temperature, yield and selectivity (Table 3). The catalytic activity of Au@CA as the epoxidation catalyst was compared with Fe_3O_4-CuO supported on mesoporous silica [22], gold nanoparticles supported on silica [23] and Ag supported on Fe_3O_4 [24]. Clean and mild reaction conditions, high yield and excellent selectivity were obtained with Au@CA compared to other catalysts represented in Table 3. The most important factor for the epoxidation reaction is the reaction temperature. The reaction was performed at room temperature with Au@CA, successfully. The importance of this work becomes clear when the results of styrene epoxidation with Au@CA as the catalyst are compared with the results of epoxidation reaction with Au@silica as the catalyst, which has difference with Au@CA at the support. Mild and green reaction conditions for Au@CA show that Au NPs supported on cellulose have high activity for the epoxidation reaction of styrene. However, the epoxidation reaction of styrene using Au@CA has advantages such as green solvent, cheep oxidant, mild reaction conditions, high yield, excellent selectivity and short reaction duration. Also, the catalyst is recyclable for six times.

In conclusion, we have demonstrated that Au@CA is an efficient catalyst for styrene epoxidation. High yield of styrene oxide was selectively obtained in short reaction duration in mild reaction conditions. Avoiding strong basic moieties and high temperatures and application of a self-controlling catalytic system which prevents from transformation of styrene oxide to acetophenone and acetaldehyde are characteristic features of this approach. H_2O as a green solvent and H_2O_2 as a green oxidant are other advantages of this report.

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