Expert Review of Chinese Chemical

ISSN:3006-0095 EISSN:3006-0109

Research Progress in Preparation of Oxidized Cellulose

Haiyan Zhu[1,2], Lixin Zhou[2], Zhenzhen Yang[3*]

1. College of Chemistry and Chemical Engineering, Zhengzhou Normal University; 2. Inner Mongolia University of Technology; 3. Shandong University of Science and Technology.

**Corresponding author:* Zhenzhen Yang, E-mail: 965874145@163.com

How to cite this paper: Haiyan Zhu, Lixin Zhou, Zhenzhen Yang. Research Progress in Preparation of Oxidized Cellulose. (2024) *Expert Review of Chinese Chemical*, 2 (**2**): 8-14.

Received: February 04, 2024
Accepted: February 12, 2024
Published: April 20, 2024

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Abstract

Cellulose is the most abundant natural polymer material in the world. Cellulose is difficult to dissolve because it contains a large number of inter molecular hydrogen bonds. Therefore, the modification of natural cellulose by chemical oxidation can expand its application field. The oxidation process of cellulose is focused on, the oxidation methods and research progress of cellulose are introduced, and further development direction of oxidized cellulose is prospected.

Keywords

oxidized cellulose; non-selective oxidation; selective oxidation

Introduction

With the progress of technology and the development of society, people's demands for energy and environmental protection are also increasing day by day. Traditional polymer materials are mostly derived from petrochemical products, are non degradable, and can cause significant harm to the natural environment [1]. Therefore, people need a renewable, safe, and pollution-free new material to replace synthetic polymer materials. Cellulose materials stand out among many materials and are increasingly being paid attention to due to their renewable, biodegradable, and environmentally friendly properties [2–4].

Cellulose itself has high crystallinity and is difficult to dissolve, which is not conducive to processing and utilization. Therefore, researchers prepared oxidized cellulose by chemical oxidation of natural cellulose [5]. Compared with natural cellulose, the main chain of oxidized cellulose introduces active groups such as aldehyde and carboxyl groups, making it have good processing performance and potential for further chemical modification [6]. At present, cellulose oxide has many applications in medical materials, sewage treatment materials, functional materials, and so on. Oxidized cellulose containing carboxyl and aldehyde groups is considered an excellent hemostatic material, and the widely used absorbable hemostatic gauze, instant gauze, is made from regenerated oxidized cellulose. In addition, oxidized cellulose is also used in hydrogel materials, thickeners, flexible electronics, cosmetics, etc. [7–9].

This article will start from the oxidation methods of cellulose, summarize the oxidation methods and research achievements of cellulose in recent years, summarize and analyze the relationship between the structure and properties of oxidized cellulose, and make prospects for the development trend of oxidized cellulose.

1 The characteristics and structure of cellulose

At room temperature, cellulose is an odorless white powder that is difficult to dissolve or melt, and has limited swelling in water. When heated above 150 ℃, dehydration and coking will occur. Under the action of NaOH/urea aqueous solution, cellulose will undergo certain dissolution, because the solution enters the crystal region of cellulose, causing swelling first and then dis-

solution. In addition, concentrated acid can decompose cellulose into glucose, and concentrated alkali reacts with it to form alkaline cellulose. Strong oxidants will oxidize it to oxidized cellulose [10–12].

The structure of cellulose is shown in Figure 1 and is a straight-chain material formed by β-1,4- glycosidic linkage to D-glucopyranose to form a straight-chain material. The degree of polymerization of natural cellulose is usually between 500 and 15000, and the relative molecular weight is between 81000 and 240000. In addition to the glucose groups at both ends of cellulose, there are three free hydroxyl groups located at positions C2, C3, and C6 on each glucose unit of the main chain. Among them, C2 and C3 are secondary hydroxyl groups, and C6 is primary hydroxyl group. The oxidation reaction of cellulose mainly occurs on the three hydroxyl groups.

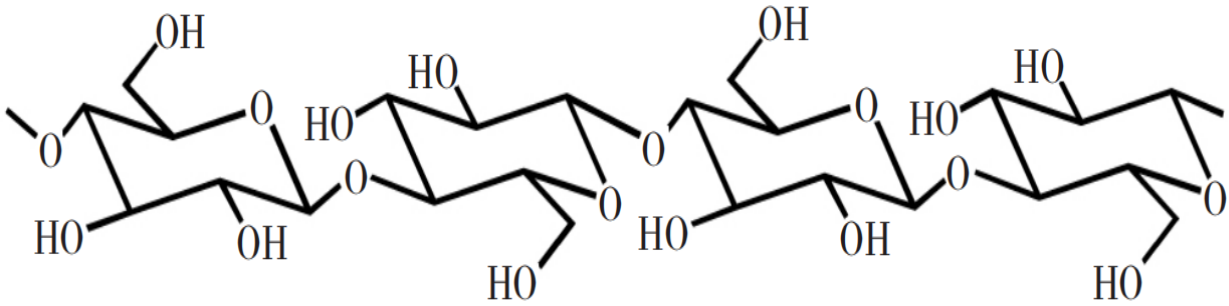


Figure 1. Cellulose structure

2 Oxidation of cellulose

Natural cellulose is entirely composed of three elements: C, H, and O, and the products of its combustion (complete oxidation) are water and carbon dioxide. In addition, cellulose also exhibits partial oxidation under the action of oxidants. The oxidation reaction of cellulose is a heterogeneous reaction. Due to the difficulty in dissolving cellulose, the oxidation reaction of cellulose generally occurs in the suspension of cellulose, and the oxidant reacts with the surface of cellulose particles. The oxidation reaction of cellulose can be divided into non selective oxidation and selective oxidation according to the different reaction positions.

2.1 Non selective oxidation

Cellulose undergoes oxidation reactions at multiple locations under the action of strong oxidants, accompanied by degradation of the main chain. In real life, the use of oxidants such as hydrogen peroxide and sodium hypochlorite to bleach fiber substances such as wood pulp and cotton fabrics is a non selective oxidation that can cause molecular chain breakage and produce various cellulose derivatives. Commonly used non selective oxidants for cellulose include peroxides, potassium permanganate, nitrates, nitrites, etc. [13–15].

The reaction of peroxide oxidation of cellulose is usually accompanied by metal ions as catalysts. Through the catalytic oxidation of metal ions and peroxides, the hydroxyl groups on cellulose are oxidized to aldehyde and carboxyl groups. Huang Xiaolei et al. [16] used Fenton reagent, a system combining hydrogen peroxide and Fe^{2+}, to perform non selective oxidation of cellulose. The experiment investigated the effects of pH value, oxidation reaction time, hydrogen peroxide dosage, and catalyst Fe^{2+} dosage on the degree of cellulose oxidation and degradation. The results showed that at a cellulose pulp concentration of 1%, with the increase of catalyst Fe^{2+} dosage, the overall content of aldehyde and carboxyl groups showed a trend of first increasing and then decreasing, and the increase in aldehyde group content was greater than that of carboxyl group. Roya Koshani et al. [17] used hydrogen peroxide and copper sulfate as catalytic oxidants to prepare rod-shaped carboxylated cellulose materials under acidic conditions, with an average length of 263nm and a width of 23nm. Yan et al. [18] prepared oxidized bacterial cellulose using sulfuric acid hydrolysis and hydrogen peroxide oxidation, which is a rod-shaped microfiber with a high crystallinity of 89.6%.

The reaction of potassium permanganate oxidizing cellulose is carried out under acidic conditions and at a relatively mild reaction temperature, oxidizing the hydroxyl groups on cellulose to carboxyl groups. Zhou et al. [19] used potassium permanganate as an oxidant and oxalic acid as a reducing agent in dilute sulfuric acid medium to prepare rod-shaped carboxylated cellulose with a length of 150-300nm and a diameter of 10-22nm in a short period of time. The yield of carboxylated cellulose prepared by this method reached 68%, with a carboxylate content of 1.58mmol/g and a crystallinity of 89.2%.

Nitrite oxidation of cellulose is a nitro oxidation method that can directly prepare carboxymethyl cellulose from a mixture of untreated cellulose, hemicellulose, and lignin. This method involves releasing nitronium ions (NO^{2+}) from nitric acid and nitrite in the presence of excess acid, which can attack the primary hydroxyl group of cellulose and produce aldehyde groups (intermediates), followed by carboxylate ester groups. Priyanka

R. Sharma et al. [20] prepared carboxylated cellulose under mild reaction conditions (50 ℃) using nitric acid and sodium nitrite as oxidants, with a carboxylate content of 1.15mmol/g.

2.2 Selective oxidation

Cellulose can undergo specific forms of oxidation reactions at specific locations under appropriate oxidation conditions (type of oxidant, reaction temperature, reaction time, etc.). According to the different oxidation sites, the selective oxidation of cellulose can be divided into selective oxidation of secondary hydroxyl groups (ring opening oxidation at C2 and C3 positions) and selective oxidation of primary hydroxyl groups (oxidation at C6 positions).

2.2.1 Selective oxidation of secondary light groups

The selective oxidation of secondary hydroxyl groups utilizes the specificity of periodate ions towards adjacent diols and similar structures, thereby introducing dialdehyde structures into cellulose chains using periodates. As shown in Figure 2, the process of obtaining dialdehyde cellulose through the oxidation of periodate is a process of opening the D-pyranose ring, and a semi acetal structure is formed between the molecular chains. Therefore, the produced dialdehyde cellulose also needs to be reduced using sodium borohydride. The specific steps for preparing dialdehyde cellulose mainly involve using periodate as an oxidant under dark conditions to oxidize the secondary hydroxyl groups at the C2 and C3 positions of cellulose to form aldehyde groups, and then reducing them with sodium borohydride. This reaction has high requirements for reaction temperature, reaction time, and other reaction conditions. If overreacted, it will cause the aldehyde group to continue to oxidize, leading to the breakage of the cellulose main chain [21–24].

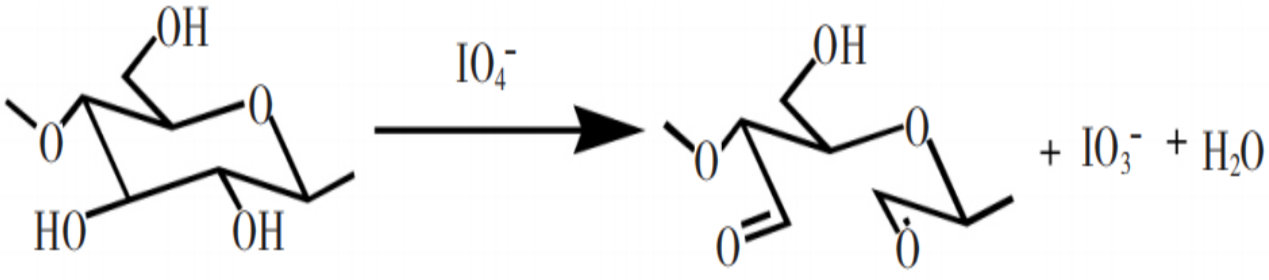


Figure 2. Schematic diagram of sodium periodate oxidized cellulose

Yang Yang et al. [25] investigated the pretreatment of wood pulp and the effect of system pH on the oxidation reaction during the oxidation of broad-leaved wood pulp with sodium periodate. The results showed that the aldehyde content of the slurry increased with the increase of oxidation process temperature, time, oxidant dosage, and slurry concentration, while the degree of polymerization showed a decreasing trend. Zhang et al. [26] investigated the effect of time on the oxidation of cellulose by sodium periodate during the reaction process. It was found that the aldehyde content of oxidised cellulose rises and the yield of oxidised cellulose decreases with the prolongation of the reaction time within a certain period of time. This is mainly due to the destruction of the β-1,4- glycosidic bond of cellulose during the oxidation of cellulose at the C2 and C3 positions by sodium periodate, which results in the reduction of the overall degree of polymerisation of cellulose and the average relative molecular mass, and at the same time, the obtaining of a number of water-soluble molecular chains, which in turn reduces the yield. Kim et al. [27] crosslinked oxidized cellulose and chitosan oxidized by sodium periodate through Schiff base reaction to obtain oxidized cellulose crosslinked chitosan. Oxidized cellulose crosslinked chitosan has excellent adsorption ability for bovine serum protein in an environment with a pH value of 5.5, and has broad application prospects in protein fixation and drug release. Sven F. Plappert et al. [28] used sodium periodate as an oxidant and reacted at 48 ℃ for 19 hours to produce dialdehyde cellulose. This type of dialdehyde cellulose has a high degree of oxidation and is soluble in hot water. The film prepared by mixing it with nano microcrystalline cellulose has high transparency, high tensile strength, and high elastic modulus, especially with excellent oxygen isolation performance. Sirvio et al. [29] found that metal chlorides have a promoting effect on the oxidation of cellulose by sodium periodate. When the ratio of metal chlorides to dehydrated glucose units (AGU) reaches 7, metal chlorides such as LiCl, $CaCl_2$, and $ZnCl_2$ can promote the oxidation of periodate at high temperatures. The reason behind this is that metal chlorides can promote the dissolution of cellulose, thereby improving oxidation efficiency. Thiangtham et al. [30] prepared a water-soluble sulfonated cellulose from sugarcane bagasse using sodium periodate oxidation and potassium metabisulfite sulfonation methods. The aqueous solution of this material has transparency, and due to the large negative charge on the surface of sulfonated cellulose, it has certain application prospects in lithium battery separators. Ruan et al. [31] prepared porous cellulose oxide beads by reacting dialdehyde cellulose obtained from sodium periodate oxidation with chitosan. These beads exhib-

ited good adsorption and desorption properties for Congo red dye at different pH values, making them an excellent chemical waste adsorption material.

2.2.2 Selective oxidation of primary light groups

There are multiple oxidation systems for the selective oxidation of primary hydroxyl groups. The main mechanism of action is to use nitrogen oxygen radicals as oxidants to oxidize the primary hydroxyl group at the C6 position of cellulose to carboxyl groups. The specific oxidation systems include the nitrogen oxide series system, sodium nitrate/sodium nitrite/phosphate system, N-hydroxyphthalimide (NHPI) system, and the famous 2, 2, 6, 6-tetramethylpiperidine nitrogen oxide radical (TEMPO) system.

The nitrogen oxide oxidation system oxidizes cellulose through nitrogen oxides in the presence of high temperature and high pressure [32]. This method has the disadvantage of slow reaction speed and producing a large amount of nitrogen-containing by-products. To address these issues, Camy et al. [33] dissolved nitrogen dioxide in a supercritical carbon dioxide solution to oxidize cellulose, achieving good results in this scheme, as shown in Figure 3. However, the presence of carbon dioxide also limits the oxidation of cellulose by nitrogen oxides. Cheng et al. [34,35] used a carbon tetrachloride solution containing 20% nitrogen dioxide to oxidize cellulose. As the oxidation time increased, the carboxyl content in the oxidized cellulose increased and the degree of polymerization decreased. This kind of oxidized cellulose has good wettability with blood and significant hemostatic function, and can be used as a medical hemostatic material.

Under certain conditions, N-hydroxyphthalimide (NHPI) generates N-oxyphthalimide radical (PINO), which can undergo oxidation reaction with the primary hydroxyl group at the C6 position of cellulose, resulting in the formation of carboxylated cellulose [36–39]. Coseri et al. [40] used N-hydroxyphthalimide as a catalyst to obtain carboxymethyl cellulose oxidized at the C6 position under the action of sodium hypochlorite and sodium bromide. Zhou et al. [41] used NHPI/Co $(OAc)_2$ as a catalyst and oxygen as an oxidant to oxidize cellulose in acetic acid. The results showed that the primary hydroxyl group at the C6 position of cellulose was converted to carboxyl group, and the degree of polymerization of cellulose slightly decreased, with almost no structural change. Biliuta et al. [42] compared the oxidation process of cellulose between NHPI system and TEMPO system. The experiment found that the NHPI system has a relatively mild oxidation of cellulose and can obtain a higher carboxyl content. The TEMPO system will to some extent lead to the degradation of cellulose during the oxidation process.

The 2, 2, 6, 6-tetramethylpiperidine nitrogen oxide radical (TEMPO) is oxidized by hypochlorite to produce nitrite ions, which then react with the primary hydroxyl group to produce carboxymethyl cellulose. The specific reaction process is shown in Figure 4.

Rahman et al. [43] catalyzed the oxidation of primary alcohol groups by using different amounts of NaClO (2-10 mmol), 0.016g TEMPO, and 0.1g NaBr. The results indicate that within the selected concentration range, with the increase of oxidants, the degree of oxidation increases, the more charges are introduced, and the carboxylic acid groups also increase, making cellulose fibrillization easier. Liu et al. [44] covalently bonded TEMPO with PA MAM dendrimers with purity of 97.2% and 93.8%, respectively, to prepare a water-soluble immobilized catalyst for selective catalytic oxidation of cellulose in aqueous solution. It was found that the immobilized water-soluble catalyst increased its catalytic activity. The catalytic activity of PAMAM-TEMPO with a purity of 97.2% was equivalent to that of free TEMPO, and it could be easily recovered by extracting the supernatant after salt precipitation with DMF. After four oxidation cycles, its catalytic performance did not decrease. Liu Borui et al. [45] selectively oxidized the primary alcohol hydroxyl groups on bamboo cellulose C6 to aldehyde or carboxyl groups using a TEM-PO/sodium hypochlorite/sodium bromide catalytic oxidation system, and further improved the carboxyl conversion rate of the primary hydroxyl groups under acidic conditions using sodium chlorite treatment. By comparing the oxidized cellulose suspensions obtained by oxidation with different NaClO concentrations, it can be concluded that different

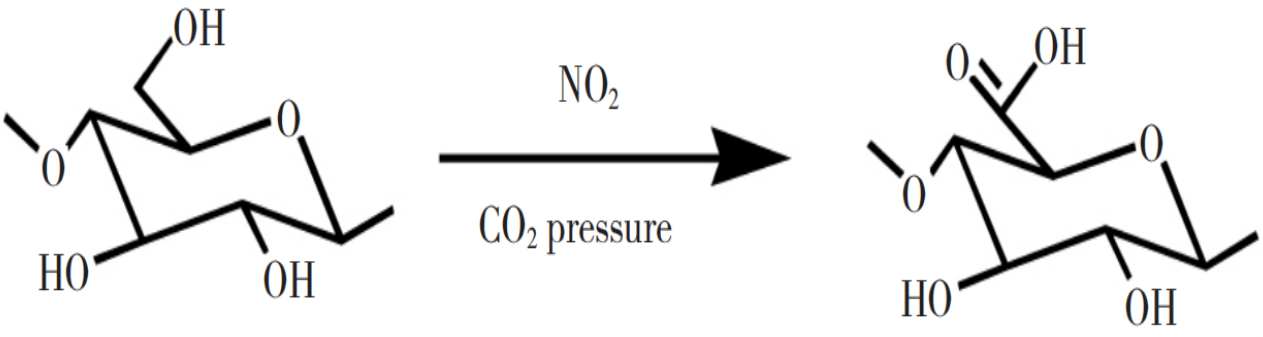


Figure 3. Schematic diagram of nitrogen dioxide oxidized cellulose

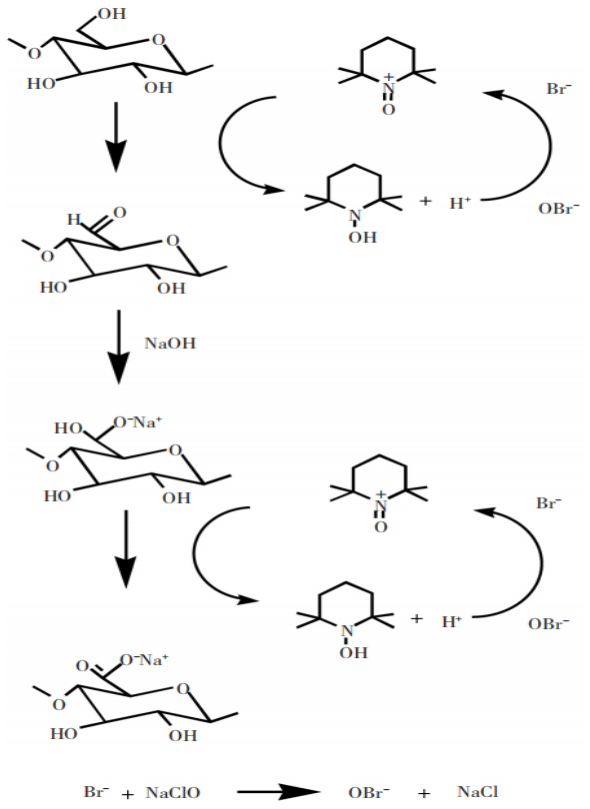


Figure 4. Schematic diagram of oxidized cellulose in TEMPO system

amounts of NaClO addition will ultimately lead to varying degrees of nanofiber formation. Within a certain range, the more NaClO is added to the unit oxidized cellulose fiber, the finer the structure of the resulting nanocellulose. Wang Liuqing et al. [46] used ultrasound coupled TEMPO/$NaClO_2$/NaClO system to prepare oxidized cellulose, and studied the effects of ultrasound time, temperature, and power on the oxidation effect during the oxidation process. The results showed that when the ultrasound power was increased from 300W to 500W, the carboxyl content of the oxidized fiber increased from 0.65mmol/g to 1.72mmol/g; When the reaction temperature increases from 40 ℃ to 60 ℃, the carboxyl content increases from 1.206 mmol/g to 1.3813 mmol/g; As the ultrasound time prolongs, the carboxyl content of oxidized cellulose shows a trend of first increasing and then decreasing. When the ultrasound time is 3 hours, the carboxyl content reaches 1.5456mmol/g. Tang et al. [47] used TEMPO to oxidize bamboo pulp fibers treated with NaOH/urea solution, with an oxidation rate of up to 91%. Yang et al. [48] prepared a composite film of oxidized cellulose graphene by mixing TEMPO oxidized cellulose with graphene. This thin film combines cellulose oxide and graphene through strong hydrogen bonding. When the graphene content is 20% (wt), the conductivity of the film reaches 568S/cm, which is expected to be applied in flexible conductive materials. Wu et al. [49] obtained negatively charged oxidized cellulose nanofibers using the TEMPO oxidation method, and combined the oxidized cellulose nanofibers with positively charged layered double hydroxides through intermolecular ionic and hydrogen bonds to obtain a composite film of oxidized cellulose layered double hydroxides with a nano intercalation structure. The film has good mechanical properties and hydrophobic flame retardant properties. Cheng et al. [50] prepared hemostatic films and sponge materials by combining cellulose oxidized by TEMPO method with sodium alginate. In vivo experiments have shown that this material can be completely biodegradable and has no inflammatory response after three weeks, making it an ideal postoperative wound hemostatic material.

3 Outlook

Cellulose, as a renewable, safe, and pollution-free natural polymer material, is receiving increasing attention in today's increasingly scarce petroleum resources and deteriorating environmental conditions. By endowing cellulose with active groups such as aldehyde and carboxyl groups through different oxidation methods, a variety of cellulose derivatives are developed to further endow cellulose with more application methods. However, the existing cellulose oxidation schemes also have many problems. The non selective oxidation using substances such as peroxides, potassium permanganate, nitrates, and nitrites has the problem of uncontrollable reaction results. We can start with the oxidation conditions (temperature, time, catalyst) to make the reaction develop in a controllable direction. Sodium periodate is the main reagent for preparing dialdehyde cellulose. Adding metal chlorides during its reaction can significantly improve oxidation efficiency. However, how to prevent excessive ring opening oxidation of cellulose is the key to the next step of research. The reaction rate of nitrogen oxide oxidation system is slow, and the by-product pollution is severe. N-hydroxyphthalimide (NHPI) is insoluble in water and requires the generation of N-oxo-phthalimide radical (PINO) under certain conditions to react. 2,2,6,6-tetramethylpiperidine nitrogen oxide radical (TEMPO) is currently a widely studied cellulose oxidation scheme, but TEMPO is expensive. Some studies have used 2-azaadamantane N-oxide (AZA DO) and its derivatives as substitutes for TEMPO to oxidize cellulose [51]. In recent years, research has shown that oxidized cellulose has important applications in many aspects such as environmental protection and medical care. Meanwhile, with further research on the oxidation mechanism of cellulose and the development of new oxidants, the preparation of oxidized cellulose will develop towards energy conservation, safety, and pollution-free directions. Due to the fact that cellulose itself is an excellent biomass material, future oxidized cellulose is expected to have more applications in the field of biology.

Author Introduction

Haiyan Zhu, master, lecturer. Research direction: Polymer synthesis

and cellulose modification.;

Lixin Zhou, master, lecturer. Research direction: Polymer synthesis and cellulose modification.;

Zhenzhen Yang, doctor, associate professor. Research direction: Modification and functionalization of biomass materials.

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