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Microwave fabrication of Cu_2ZnSnS_4 nanoparticle and its visible light photocatalytic properties

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Abstract

Cu_2ZnSnS_4 nanoparticle with an average diameter of approximately 31 nm has been successfully synthesized by a time effective microwave fabrication method. The crystal structure, surface morphology, and microstructure of the Cu_2ZnSnS_4 nanoparticle were characterized. Moreover, the visible light photocatalytic ability of the Cu_2ZnSnS_4 nanoparticle toward degradation of methylene blue (MB) was also studied. About 30% of MB was degraded after 240 min irradiation when employing Cu_2ZnSnS_4 nanoparticle as a photocatalyst. However, almost all MB was decomposed after 90 min irradiation when introducing a small amount of H_2O_2 as a co-photocatalyst. The enhancement of the photocatalytic performance was attributed to the synergetic effect between the Cu_2ZnSnS_4 nanoparticle and H_2O_2. The detailed photocatalytic degradation mechanism of MB by the Cu_2ZnSnS_4 was further proposed.

Keywords: Cu_2ZnSnS_4; Microwave fabrication; Photocatalyst

Background

Organic dyes widely used in textile and plastic industries are one of the chief sources of contaminants in wastewater. They have induced serious environmental problems due to their potential toxicity to living organisms. Degradation and total removal of such contaminants are keys to ensuring a protected environment. A photocatalytic technique is considered to be a promising method for treating organic dyes in wastewater [1]. However, an obvious challenge for degradation of organic dyes is that most photocatalysts, such as TiO_2 or $BiVO_4$ [2,3], are only effective in the UV range. To broaden their light absorption range, various methods including dye sensitizing [4], metal doping [5] non-metal doping [6,7], and noble metal decorating [8] have been developed. However, stable and efficient dyes are rare and expensive. Moreover, dopant impurity atoms in photocatalysts often serve as recombination centers for photogenerated holes and electrons [9]. To avoid these problems, great efforts have also been put into the development of alternative undoped photocatalysts which work under visible light irradiation. Until now, many materials with attractive visible light photocatalytic performance, such as $Bi_2TiO_4F_2$ [10], Bi_2O_3 [11], $AgNbO_3$ [12], and graphene oxide enwrapped Ag/AgX (X = Br, Cl) nanocomposite [13] have been investigated. However, the supply of rare elements of Ag, Bi, and Nb is a critical issue for widespread use. Thus, it is crucial to investigate alternative cost-effective visible-light-driven photocatalysts.

Cu_2ZnSnS_4 is a direct bandgap p-type semiconductor with a high optical absorption coefficient of about 10^5 cm^{-1} [14,15]. Its elements are environmentally friendly and abundant in the earth's crust. As its bandgap is around 1.5 eV, it can absorb most of the visible light. It has been reported that Cu_2ZnSnS_4 possesses high photocorrosion resistance in air and aqueous solution [16]. Both of these superior properties of Cu_2ZnSnS_4 enrich its potential use in solar-energy-related applications.

In this work, we have fabricated the Cu_2ZnSnS_4 nanoparticle by a facile microwave fabrication method. The advantages of this method are the following: it is economical of time and cost effective. The crystal structure and surface morphology of the prepared Cu_2ZnSnS_4 nanoparticle were characterized. Moreover, the photocatalytic performance of the Cu_2ZnSnS_4 nanoparticle toward the degradation of methylene blue (MB) under visible light irradiation was also investigated. The Cu_2ZnSnS_4 nanoparticle showed noteworthy visible light photocatalytic ability.

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Methods

The Cu_2ZnSnS_4 nanoparticle was synthesized by a facile microwave fabrication method. $Cu(CH_3COO)_2 \cdot H_2O$, $Zn(CH_3COO)_2$, $Sn(CH_3COO)_2$, and thiocarbamide with a molar ratio of 2:1:1:4 were employed as source materials. All the reagents were analytically pure and bought from Sinopharm Chemical Reagent Co., Ltd, Shanghai, China. Typically, 1.123 g of the source materials was dissolved in 20 mL ethylene glycol solution as precursor. Then the precursor was stirred gently and heated in a microwave reactor (MCR-3, Gongyi City Yuhua Instrument Co., Ltd, Gongyi City, China) at 180°C for 10 min. After the vacuum filtration and drying process, the Cu_2ZnSnS_4 nanoparticle sample was obtained.

The crystal structure of the Cu_2ZnSnS_4 nanoparticle was investigated by X-ray diffraction (XRD; D/max-2200/PC, Rigaku, Tokyo, Japan) and Raman spectroscopy (Senterra, Bruker, Billerica, USA). The surface morphology and microstructure of the Cu_2ZnSnS_4 were measured by scanning electron microscopy (SEM; JSM 5800LV, JEOL, Tokyo, Japan) and transmission electron microscopy (TEM; JEM-2100, JEOL, Tokyo, Japan).

The photocatalytic properties of the prepared Cu_2ZnSnS_4 nanoparticle were investigated by employing MB as a model dye. The Cu_2ZnSnS_4 nanoparticle (20 mg) was dispersed in 100 mL of MB aqueous solution (10 mg/L). Prior to irradiation, the MB solution over the catalyst was gently stirred in the dark for 30 min to reach equilibrium adsorption state. Then the solution was illuminated with a 100-W xenon light source (Shanghai Yaming Lighting Co., Ltd., Shanghai, China). The concentration change of MB was monitored by measuring UV-vis absorption of the extracted MB solution at regular intervals. The characteristic peak absorbance of MB at 665 nm was used to determine its concentration. In addition, the photocatalytic properties of the Cu_2ZnSnS_4 nanoparticle with the assistance of 0.1 mL H_2O_2 (30% aqueous solution) were further investigated in the same measurement process. For comparison, a control experiment without adding Cu_2ZnSnS_4 and H_2O_2 was also carried out.

Results and discussion

The crystal structure of the prepared Cu_2ZnSnS_4 nanoparticle is shown in Figure 1. The observed diffraction peaks at $2\theta = 28.48°$, 32.77°, 47.38°, and 56.26° correspond to the Cu_2ZnSnS_4 crystal planes (112), (200), (220), and (312), which match well with the standard XRD data file of Cu_2ZnSnS_4 (JCPDS No. 26-0575). No other crystalline by-products were observed in the pattern, suggesting that the as-prepared sample was pure Cu_2ZnSnS_4. Additionally, the strong relative intensity of the (112) and (220) lines indicates the Cu_2ZnSnS_4 nanoparticle is preferentially oriented in the (200) and (110) directions during the growing process.

In addition, it has been reported that the spectra of Cu_2ZnSnS_4 and β-ZnS are very similar in the XRD

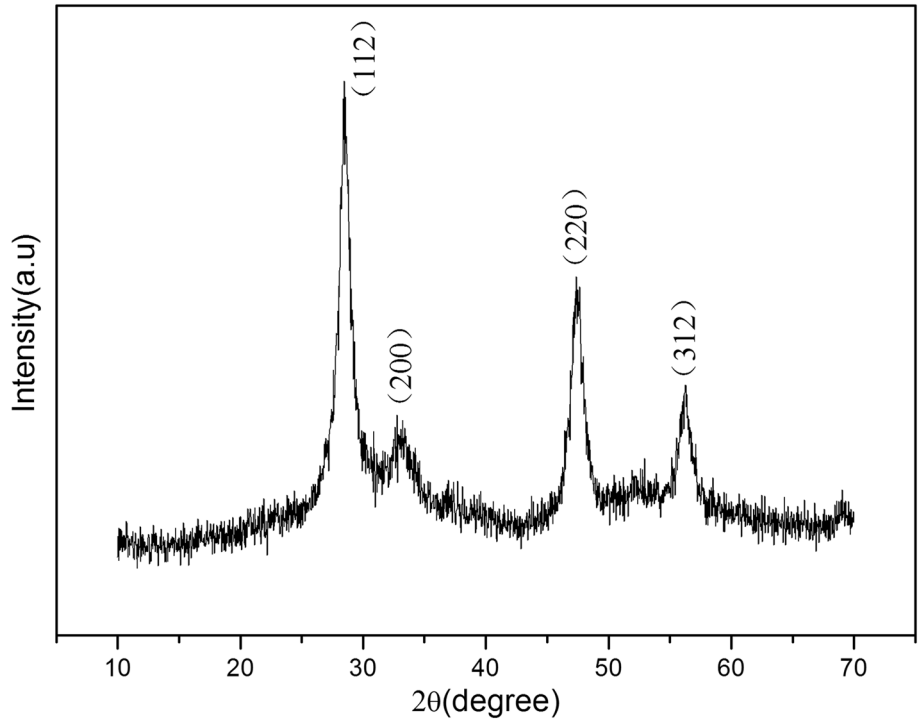

Figure 1 XRD pattern for the Cu_2ZnSnS_4 nanoparticle. The peaks have been indexed to kesterite Cu_2ZnSnS_4 (JCPDS No. 26-0575).

analysis results [17]. Raman spectroscopy analysis is a feasible method to distinguish Cu_2ZnSnS_4 from β-ZnS [18]. Therefore, we employed Raman spectroscopy to further confirm the structure of the prepared Cu_2ZnSnS_4 nanoparticle. A Raman spectrum of the prepared Cu_2ZnSnS_4 nanoparticle over the wave number range of 200 to 450 cm^{-1} is shown in Figure 2. There is an intensive peak located at approximately 331 cm^{-1}, which suggests the existence of Cu_2ZnSnS_4 [17,19]. The characteristic peaks of β-ZnS located at 348 and 356 cm^{-1} are not observed in the spectrum [20], indicating the absence of β-ZnS.

Surface morphology and microstructure of inorganic semiconductor materials are of vital importance to their optoelectronic properties. Accordingly, the surface morphology of the Cu_2ZnSnS_4 nanoparticle was studied by SEM. Figure 3a demonstrates a representative surface morphology of the Cu_2ZnSnS_4 nanoparticle. It can be seen that the Cu_2ZnSnS_4 nanoparticle possesses similar sizes in diameter and packs uniformly. The average diameter of the Cu_2ZnSnS_4 nanoparticle is approximately 31 nm calculated from randomly selected 100 nanoparticles. High-resolution transmission electron microscopy (HRTEM) was further employed to investigate the microstructure of the Cu_2ZnSnS_4 nanoparticle. Figure 3b shows a typical HRTEM image of the Cu_2ZnSnS_4 nanoparticle. The interplanar spacing of 2.7 Å corresponds to the (200) plane of kesterite Cu_2ZnSnS_4. The selected area electron diffraction (SAED) pattern shown in Figure 3c suggests the polycrystalline nature of the nanoparticle.

To evaluate the photocatalytic performance, we analyzed the decomposition of the (MB) dye in aqueous solution over the Cu_2ZnSnS_4 nanoparticle under visible light irradiation. Figure 4a presents the time-dependent absorption spectra of MB degradation over the Cu_2ZnSnS_4 nanoparticle upon visible light irradiation. The five curves in the pattern are the UV-vis spectra of MB solutions extracted at 0 min, 30 min, 60 min, 150 min, and 240 min. It can be observed that the absorbance peak at 665 nm, which is the characteristic absorption peak of MB, reduced slowly with increasing irradiation time. After 240 min, only about 30% of MB was degraded. In addition, it was difficult to further degrade MB by increasing the irradiation time. However, with the addition of 0.1 mL H_2O_2 (30% aqueous solution), as shown in Figure 4c, almost all MB was degraded after 90 min irradiation. In general, peroxymonosulfate, peroxydisulfate, and H_2O_2 are often employed to assist in evaluating the photocatalytic properties of semiconductor materials. Both peroxymonosulfate and peroxydisulfate can be driven by visible light for photochemical oxidation [21], while H_2O_2 can hardly be activated [22]. Additionally, as a typical organic pollutant, MB is stable under visible light irradiation if no photocatalysts are involved. Therefore, the degradation of MB molecules was attributed to the synergetic effect of Cu_2ZnSnS_4 nanoparticle and H_2O_2. The H_2O_2 enhanced the photocatalytic ability through an

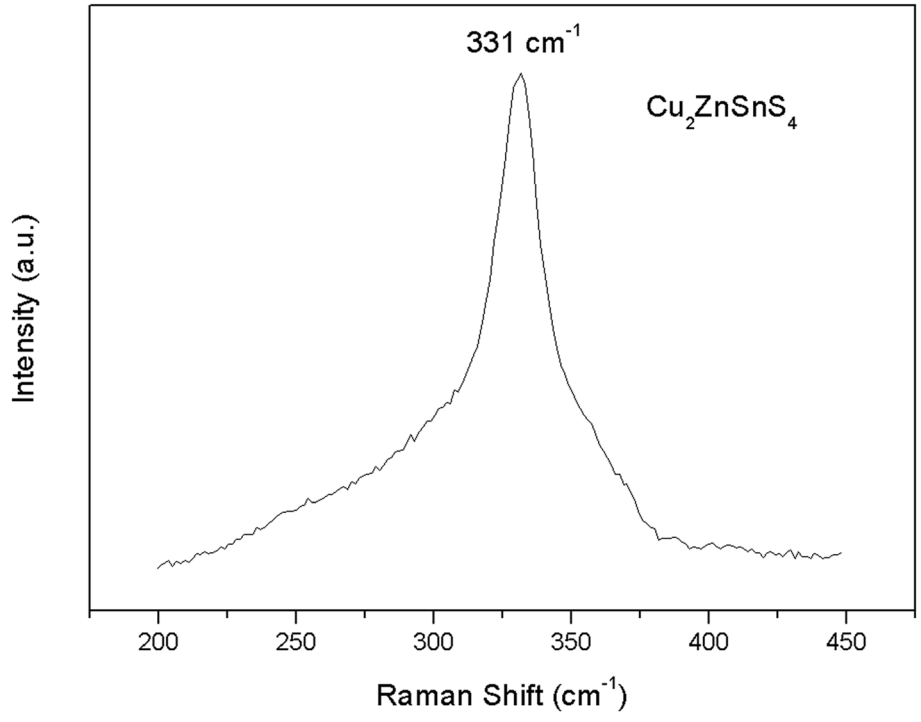

Figure 2 Raman spectra of the prepared Cu_2ZnSnS_4 nanoparticle.

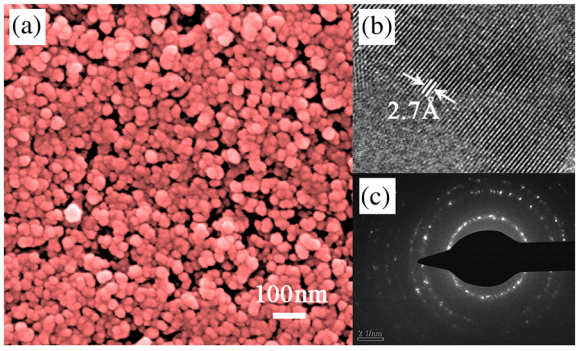

Figure 3 SEM, HRTEM, and SAED images of the prepared Cu_2ZnSnS_4 nanoparticle. (a) Scanning electron microscopy (SEM), **(b)** high-resolution transmission electron microscopy (HRTEM), and **(c)** selected area electron diffraction (SAED) images of the prepared Cu_2ZnSnS_4 nanoparticle.

efficient charge transfer of the photogenerated carriers from the surface of the Cu_2ZnSnS_4 nanoparticle to the MB molecule. Figure 4b,d illustrates the curves of C/C_0, where C_0 is the initial concentration of MB and C is the concentration of MB at time t. Insets in Figure 4b,d present the curve of the corresponding $\ln(C_0/C)$ versus irradiation time. No linear relationship between irradiation time and $\ln(C_0/C)$ can be observed when employing the Cu_2ZnSnS_4 as a photocatalyst solely. However, with the assistance of H_2O_2, a linear relationship between irradiation time and $\ln(C_0/C)$ is well established, suggesting that the photodegradation of MB over the Cu_2ZnSnS_4 nanoparticle and H_2O_2 proceeded through the pseudo-first-order kinetic reaction [23]. The first-order reaction rate constant k_1 was 0.04 min^{-1}, which is comparable to that of TiO_2-C hybrid aerogel photocatalysts ($0.01 \sim 0.06\ min^{-1}$) toward the degradation of MB driven by UV light irradiation [24].

According to the experiment results and previous reports, the photocatalytic degradation mechanism by the Cu_2ZnSnS_4 nanoparticle under visible light irradiation was illustrated in Figure 5 and proposed as follows:

$$Cu_2ZnSnS_4 \xrightarrow{\text{visible light}} Cu_2ZnSnS_4\left(e_{cb}^- + h_{vb}^+\right) \quad (1)$$

When the photogenerated carriers emigrate to the surface of the Cu_2ZnSnS_4 nanoparticle, the generated $Cu_2ZnSnS_4\left(h_{vb}^+\right)$ provides holes, decomposing the absorbed contaminant.

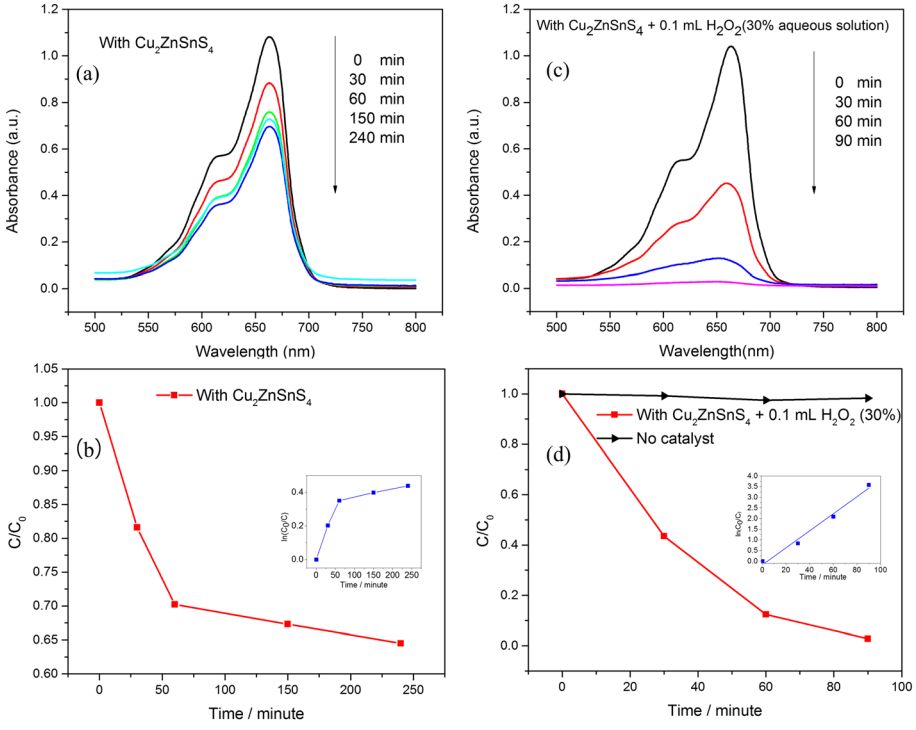

Figure 4 Photocatalytic activity of the Cu_2ZnSnS_4 nanoparticle toward the photodegradation of methylene blue (MB). (a) Time-dependent UV-vis absorbance spectra of the MB solution using the prepared Cu_2ZnSnS_4 nanoparticle as a photocatalyst. **(b)** Curves of the degradation rate of the MB dye with the prepared Cu_2ZnSnS_4 nanoparticle (C_0 is the initial concentration of MB; C is the reaction concentration of MB at time t). The inset shows the $\ln(C_0/C)$ versus time curve of the photodegradation of MB. **(c)** Time-dependent UV-vis absorbance spectra of the MB solution using the prepared Cu_2ZnSnS_4 nanoparticle and 0.1 mL H_2O_2 as photocatalysts. **(d)** Curves of the degradation rate of the MB dye with the prepared Cu_2ZnSnS_4 nanoparticle and 0.1 mL H_2O_2 as photocatalysts. The inset presents the $\ln(C_0/C)$ versus time curve of the photodegradation of MB.

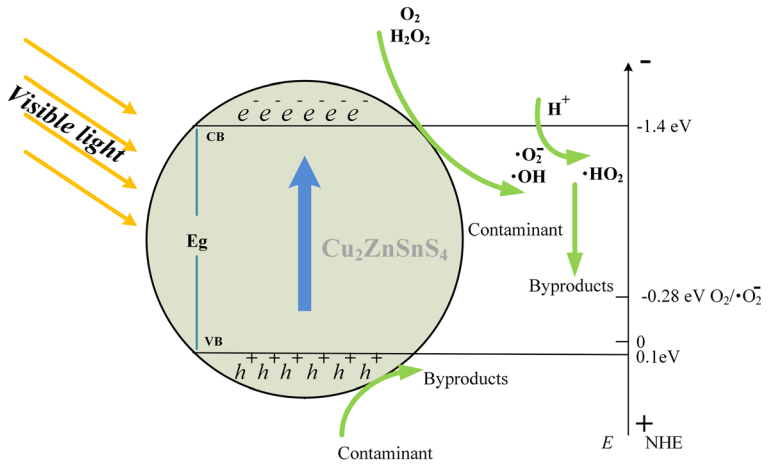

Figure 5 Schematic diagram for charge carrier separation and photocatalytic contaminant decomposition on Cu_2ZnSnS_4 photocatalyst under visible light irradiation.

$$Cu_2ZnSnS_4\left(h^+_{vb}\right) + \text{contaminant} \rightarrow \text{degraded products} \quad (2)$$

However, due to the top of the valence band of Cu_2ZnSnS_4 (+0.1 eV versus NHE) is lower than those of $\cdot OH/H_2O$ (+2.27 eV) and $\cdot OH/OH^-$ (+1.99 eV), the Cu_2ZnSnS_4 nanoparticle cannot further degrade the MB with increasing the irradiation time. More recently, Yu *et al.* [25] have reported that a noble metal such as Au or Pt can greatly improve the photocatalytic ability of the Cu_2ZnSnS_4 nanoparticle. The enhancement is attributed to surface plasmon resonance (SPR) effect, which can notably reduce the carrier recombination rate on the surface of the Cu_2ZnSnS_4 nanoparticle. In our work, with the addition of a small amount of H_2O_2, the generated Cu_2ZnSnS_4 $\left(e^-_{cb}\right)$ can react with the added H_2O_2, generating $\cdot OH$, and subsequently photodegrade the absorbed contaminant.

$$H_2O_2(\text{added}) + Cu_2ZnSnS_4\left(e^-_{cb}\right) \rightarrow \cdot OH + OH^- \quad (3)$$

$$\cdot OH + \text{contaminant} \rightarrow \text{degraded products} \quad (4)$$

H_2O_2, as an efficient electron scavenger and a source of $\cdot OH$ with high oxidizing ability, was added here to assist the photodegradation of the contaminant. However, an excess amount of H_2O_2 will decrease the photocatalytic activity [26]. As shown in Equation 5, the excess H_2O_2 scavenges the beneficial OH generating a much weaker hyperoxyl radical of $HO^{\bullet}_2$.

$$H_2O_2 + \cdot OH \rightarrow HO^{\bullet}_2 + H_2O \quad (5)$$

Besides, the $HO^{\bullet}_2$ will further react with the remaining $\cdot OH$ forming ineffective oxygen and water.

$$HO^{\bullet}_2 + \cdot O \rightarrow H_2O + O_2 \quad (6)$$

Conclusions

In summary, the Cu_2ZnSnS_4 nanoparticle was successfully synthesized by a facile microwave fabrication method. The prepared Cu_2ZnSnS_4 nanoparticle exhibited a polycrystalline structure with an average diameter of approximately 31 nm. The photocatalytic performance of the Cu_2ZnSnS_4 nanoparticle toward degradation of MB in aqueous solution was also investigated. Due to the top of the valence band of Cu_2ZnSnS_4, pure Cu_2ZnSnS_4 nanoparticle showed a poor visible light photocatalytic ability. However, when employing a small amount of H_2O_2 as electron scavenger, the photocatalytic performance was greatly enhanced. The first-order reaction rate constant k_1 toward the degradation MB reached as high as 0.04 min^{-1}. The synergetic effect between the Cu_2ZnSnS_4 nanoparticle and H_2O_2 was a key to promote the photodegradation efficiency.

Competing interests
The authors declare that they have no competing interests.

Authors' contributions
ZHZ formulated the idea of investigation and drafted the manuscript. PAZ prepared the Cu_2ZnSnS_4 nanoparticles. YLL and AE have taken part in acquisition and interpretation of data. HNJ, JW, and HDL directed the research and made corrections to the manuscript. ZMW supervised the study. All authors have read and approved the final manuscript.

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