Synthesis of ZnWO₄ Electrode with tailored facets: Deactivating the Microorganisms through Photoelectrocatalytic methods

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Abstract: The exotic invasive species from the ballast water in the ship will bring about serious damages to ecosystem. Photocatalyst films have been widely studied for sterilization. In this study, ZnWO₄ with different exposed facets was synthesized by hydrothermal method, and ZnWO₄ film electrodes have been applied in ballast water treatment through the electro-assisted photocatalytic system. Then the samples were investigated by X-ray diffraction (XRD), X-ray photo-electron spectroscopy (XPS), Field emission on scanning electron microscopy (FE-SEM), Transmission electron microscopy (TEM), UV-vis diffuse reflectance spectroscopy (DRS), BET specific surface area analysis, Fourier transform infrared (FT-IR) and Electrochemical impedance spectra (EIS). ZnWO₄ with an appropriate exposure of (0 1 1) facets ratio exhibited the best photocatalytic and photoelectrocatalytic activities. The microorganisms deactivated completely in 10 min by ZnWO₄ films with 3 V bias. The mechanisms of (0 1 1) facets enhanced the photocatalytic and photoelectrocatalytic activities which were deduced based on the calculated result from the first principles. Simultaneously, appropriate exposed facets and applied bias could reduce the recombination of the photogenerated electron-hole pairs, and improve the photocatalytic activities of ZnWO₄.

Keywords: Photoelectrocatalysis; ZnWO₄ films; Ballast water; Microorganism; first principle calculation; Exposed (0 1 1) facets

1. Introduction

The ballast waters need to be injected and discharged in order to provide needed stability and maneuverability when the ships are moving. Current data shows that 3-5 billion tons of ballast water is transferred from ships yearly [1]. The organisms in ballast water can spread to a new environment, becoming invasive species. These external species will seriously threaten the ecosystem and human activities [2]. Therefore, the International Maritime Organization (IMO) prescribes that all cargo ships must have a system for treating ballast water aimed at preventing or reducing these problems [3]. In those studies, some works indicate that the hydroxyl radical ($\cdot\text{OH}$) with high oxidation potential has an excellent bactericidal effect, which is a sound way to treat ballast water [4-5].

For our best knowledge, hydroxyl radical ($\cdot\text{OH}$) will be generated easily in photocatalysis reaction systems, which may be used in the process of ballast water discharge [6-10]. Researchers found that some of these photocatalysts are active for deactivation of bacteria [11-12]. ZnWO_4 as a photocatalytic material has a wide application prospect in bactericidal effects due to its high oxygen evolution potential [13-14]. Hydroxyl radical ($\cdot\text{OH}$) generated by ZnWO_4 has a stronger oxidation ability than TiO_2 [15]. So far, the applications of ZnWO_4 in the photocatalysis have been greatly limited due to the low efficiencies resulted from the easy recombination of photogenerated charge carriers. Many researchers do a lot of works to improve the separation efficiency of hole and electron.

According to our update, there are four methods to enhance photocatalytic activities of ZnWO_4 . (1) Forming heterojunction, such as: $\text{BiOBr}/\text{ZnWO}_4$ [16], $\text{In}_2\text{S}_3/\text{ZnWO}_4$ etc. [17]; (2) Ions doping: Er^{3+} [18], Sn^{2+} [19]; (3) Exposed different crystal facets [20-21]; (4) Electro-assisted photocatalytic activity [22-23]. For the photocatalytic activities test, ZnWO_4 can achieve great effects on organic decomposition: Methyl Orange [24-25], Phenol [26], Methylene Blue [27-28], 4-nitrophenol, 4-methoxybenzyl alcohol [29], Auramine O [30], 4-Chlorophenol [31] and AR18 [32]. Despite this progress, the efficiencies are still inadequate and the mechanisms for enhanced ZnWO_4 activity in the theoretical calculations need to be further discussed. For all we know, there are few reports on deactivated microorganism by ZnWO_4 .

In this work, ZnWO_4 photocatalyst film electrodes have been applied in ballast water treatment. The detailed process, in which exposed crystal facets and photoelectrocatalytic methods were integrated, was designed to improve the efficiencies. ZnWO_4 photocatalysts with different exposed facets were synthesized by the hydrothermal method at different pH value condition. Microorganisms (chlorella)

were employed as the probe reaction to test the photocatalytic and photoelectrocatalytic activity of the ZnWO_4 films. ZnWO_4 with an appropriate exposure ratio of (0 1 1) facets exhibited greatly enhanced activity in the photocatalytic and photoelectrocatalytic sterilization (chlorella). Then the mechanisms are investigated from the first principles calculations.

2. Experimental

2.1 Preparation of ZnWO_4

$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ (molar ratio of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ to $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ 1:1) were mixed in 80mL deionized water. Adjusting the pH value to a specific condition using HNO_3 or $\text{NH}_3 \cdot \text{H}_2\text{O}$ solution. The mixture was transferred into a reaction kettle after ultrasonication for 30 min. The reactors were heated at 180°C for 24h. Then the obtained samples were washed by distilled water three times. Finally the collected samples were further dried in an oven at 80°C for 4h.

2.2 Preparation of the ZnWO_4 film electrodes

The ZnWO_4/ITO (indium-tin oxide glass) film electrodes were prepared using the coating method. First, 0.1g ZnWO_4 and 1mg XC-72 were dissolved in 1000 μL methanol, 7000 μL distilled water and 3000 μL polytetrafluoroethylene (PTFE). The slurry was mixed by ultrasonication for 10min. Then, 600 μL slurry was applied onto ITO glass (60 $\times$ 20mm). Finally the ITO glasses were dried at 60°C for 2h in air. The carbon black, XC-72, used only as conductive material can improve the electrical conductivity of the ZnWO_4 films electrode. PTFE acts as the film former agent [26].

2.3 Experiment of Photocatalytic and photoelectrocatalytic activities

The photocatalytic and the photoelectrocatalytic activities were evaluated by deactivating the chlorella in seawater. The conventional three-electrode cell system connected with the working electrodes (ZnWO_4 film, active area of 3 cm^2), the counter electrode (Ti, 30mm in length and 10mm in width) and the reference electrodes (calomel electrode). The working electrodes were irradiated under UV light irradiation (12W, 254nm). Raw and treated ballast water (150mL) with an initial chlorella concentration of 1×10^4 cell/mL was sampled in triplicate at certain time intervals to numerate the concentration of the chlorella [33]. The concentrations of the microorganisms were enumerated using a total count method under a biological microscope [34].

To investigate the photogenerated holes and electrons separation efficiency, electrochemical impedance spectra (EIS) were tested in seawater solution by an electrochemical workstation (VMP3 Princeton Research). The reference electrodes was calomel electrode and the counter electrodes was titanium. ZnWO_4 films were used as working electrodes. The 12W Ultraviolet lamp with 254 nm wavelength was used as light source [35-36].

2.4 Characterization

The crystalline structures were characterized by X-ray diffraction (XRD) with CuK_α radiation on Rigaku DMAX⁺ Ultima⁺ diffractometer. The chemical composition of the film electrodes were studied by X-ray photoelectron spectroscopy (XPS) measurements with AlK_α radiation on Thermo Escalab250 XPS system. The morphology was characterized by the field emission on scanning electron microscope (FE-SEM) on SUPRA 55 SAPPHIRE. The crystal structures were investigated by transmission electron microscopy (TEM) on JEOL JEM-2100 instrument. The photo properties of the samples were studied by UV-vis diffuse reflectance spectroscopy (DRS) on TU-1901 UV-vis spectrophotometer. BaSO_4 was used as the reflectance standard. The N_2 adsorption and desorption of catalysts were monitored by WBL 810. The hydrogen-related defects were examined by FT-IR spectrometer (PerkinElmer Frontier).

3. Results and discussion

Fig. 1 The deactivation rate of Chlorella in the seawater under UV light (12W, 254nm) (a), ZnWO₄ (pH 9) under different bias potential (b) and all samples under 3 V bias potential (c); EIS of ZnWO₄ film electrodes at 0 V (d), ZnWO₄ (pH 9) under different bias potential (e) and all samples under 3 V bias potential (f) with UV light on.

Total count method was used to evaluate the deactivation ratio of chlorella by the ZnWO₄ film electrodes under different experimental conditions. **Fig. 1(a)** shows the data for deactivation ratio of chlorella under UV light irradiation. pH value had a significant effect on the photocatalytic activities. The deactivation ratio were 12%, 43%, 100% and 65%, respectively in 30 min, for the samples prepared at pH 4, 6, 9 and 12. The photocatalytic activities of ZnWO₄ films were enhanced with the pH

value increase when the pH value was below 9. ZnWO_4 prepared at pH 9 showed the highest deactivation efficiency. However, as the pH value further increased, the activity decreased.

Fig. 1(b) exhibits the deactivation ratio of the photoelectrocatalytic deactivation of chlorella at different bias: 1, 2, 3 and 4 V. The efficiency of deactivation increased as the bias potential increased. At the potential of 3 and 4 V, the deactivation ratio can reach 100% in 10min. Therefore, 3 V bias potential was the best experiment condition to fulfill the consideration energy efficiency.

The photoelectrocatalytic sterilization at 3 V bias potential for all samples has shown in **Fig. 1(c)**. The activities have been significantly improved for all samples in comparison of photocatalytic activities. The deactivation ratio can reach 100% in 10 min by the ZnWO_4 films obtained at pH 9, which increase to 3 times as a photocatalytic process. As a consequence, a suitable pH value could not only improve the photocatalytic activities but also enhance the photoelectrocatalytic activities. The effect of pH value for activities will be discussed subsequently.

Electrochemical impedance spectra Nyquist tests have been applied widely in demonstrating the separation efficiency of electrons and holes of photocatalysts [37]. EIS data under different bias potential were illustrated in **Fig. 1(d)-(f)**. When the pH value below 9, the radius of the arc decreased gradually as the pH value increased. ZnWO_4 obtained at pH 9 shows the smallest arc radius for both photocatalytic and photoelectrocatalytic process. The smaller radius of the circular arc means the lower resistance of the interfacial which will cause the higher separation efficiency of the electron-hole pairs [38]. As we can see from **Fig. 1(d)**, there was one radius on the EIS Nyquist plot, which indicated that the process of photocatalytic deactivation of chlorella was an electrode reaction process [39]. EIS Nyquist plots of photoelectrocatalytic process (pH 9) were shown in **Fig. 1(e)**. As the voltage of applied bias increased the radius of the arc decreased gradually. This result indicated the bias potential can accelerate the rate of charge transfer. **Fig. 1(f)** shows that ZnWO_4 film (pH 9) exhibited a smaller radius than the other samples under UV light and 3 V bias potential. Compared with **Fig. 1(d)**, it has been found that the arc shape was different. This denotes that the separation of electron-hole pairs was very efficient. Furthermore, the diffusion of reactants to the electrode interface is another factor determining the reaction rate. For this work, the charge in ZnWO_4 (pH 9) would be quickly moved to the Ti electrode through the solid/liquid interface, which would inhibit charge recombination [40].

The reason the sample prepared at a pH value of 9 showed the highest photocatalytic and photoelectrocatalytic activity is the efficient separation of electron-hole pairs. This mechanism will be explained from its structure characterization.

Fig. 2 XRD patterns for the as- prepared samples at different pH value

Fig.2 showed XRD patterns for the as-prepared samples at different pH value. $\text{WO}_3(\text{H}_2\text{O})_{0.33}$ was synthesized when the $\text{pH}=4$. The peaks at 23.07° , 28.11° , 36.99° corresponding to 0.385nm , 0.317nm , 0.243nm , were indexed as $(0\ 0\ 2)$, $(2\ 2\ 0)$, $(0\ 4\ 2)$ (JCPDS 72-0199). At a higher pH value ($\text{pH}\geq 6$) the crystal phase of ZnWO_4 appeared. The diffraction angles at 15.00° , 19.12° , 23.78° , 24.25° , 30.56° , 36.32° , corresponded to 0.576nm , 0.470nm , 0.370nm , 0.367nm , 0.292nm , 0.247nm , which can be assigned to $(0\ 1\ 0)$, $(1\ 0\ 0)$, $(0\ 1\ 1)$, $(1\ 1\ 0)$, $(1\ 1\ 1)$, $(0\ 0\ 2)$ facets of ZnWO_4 (JCPDS 73-0554) [41]. The XRD analysis shows that the $\text{WO}_3(\text{H}_2\text{O})_{0.33}$ samples possess orthorhombic structure and ZnWO_4 possess monoclinic structure.

Fig. 3 X-ray photoelectron survey (a), high resolution XPS spectra of Zn 2p (b), O 1s (c), W 4f (d) and C 1s (e) for ZnWO₄ film prepared at pH 9

X-ray photoelectron spectroscopy (XPS) was performed on the film surfaces of ZnWO₄ films to determine the elemental composition. The survey XPS spectrum (**Fig. 3(a)**) reveals that the ZnWO₄ films obtained at pH 9 were mainly composed of Zn, O, W and C. **Fig. 3 (b)** shows the peaks at 1021.8eV and 1044.8eV can be attributed to Zn 2p_{3/2} and Zn 2p_{1/2} respectively, these result indicated that the valence of Zinc in ZnWO₄ is +2. The peaks at 531.8eV can be corresponded to O 1s (**Fig. 3 (c)**). The peaks at 31.3eV and 33.5eV can be attributed to W 4f_{7/2} and W 4f_{5/2} (**Fig. 3 (d)**) of ZnWO₄. The binding energy of C_{1s} was 281.4eV (**Fig. 3(e)**), which could be characteristic of the C element in the XC-72.

Fig. 4 represents the FE-SEM image of the samples synthesized in the pH range of 4-12. The catalysts exhibited different microstructures by adjusting the pH value. From **Fig. 4 (a)** WO₃(H₂O)_{0.33} revealed irregular layer structure. ZnWO₄ nanorods with a length of 50 nm and width around 30nm can be obviously observed in **Fig. 4 (b)**. **Fig. 4 (c)** exhibited nano-sized bars with an average length of approximately 200nm and width of 50nm. The morphologies of ZnWO₄ obtained at pH 12 revealed bulk and bar structures **Fig. 4 (d)**. We speculate that different microstructure morphologies were attributed to different preferred orientation growths.

Fig.4 FE-SEM images of ZnWO_4 prepared at different pH: (a) pH 4 ($\text{WO}_3(\text{H}_2\text{O})_{0.33}$); (b) pH 6; (c) pH 9; (d) pH 12

Fig. 5 TEM and HRTEM images of the as- prepared samples at different pH value: (a), (e) pH 4; (b), (f) pH 6; (c), (g) pH 9; (d), (h) pH 12

In order to investigate the preferential orientation growth, TEM and HRTEM were conducted. The TEM images of ZnWO_4 prepared at different pH values were shown in **Fig. 5 (a)-(d)**, these data were in line with FE-SEM images. The clear lattice fringes were revealed in **Fig. 5 (f)**. The spacing of the lattice fringe was 0.576nm,

which is indexed for (0 1 0) of ZnWO₄. A lattice space of 0.370nm determined by HRTEM analysis (**Fig. 5(g)-(h)**) was identified as the (0 1 1) facet of ZnWO₄. According to experiment results, the ZnWO₄ exposed (0 1 0) facets under weakly acid conditions, exposed (0 1 1) facets under alkaline condition. ZnWO₄ exposed (0 1 1) facets exhibited better deactivation performance. The reasons will be analyzed on the basis of experimental data and the first principles calculation.

The UV-vis diffuse reflectance spectroscopy (DRS) and plots for $(\alpha h\nu)^2$ versus energy ($h\nu$) of ZnWO₄ were shown in **Fig. 6**. The absorption edge of ZnWO₄ (pH 9) is 340nm, which indicated that ZnWO₄ can be used as UV-driven photocatalysts. The band gap energy of ZnWO₄ was calculated by the equation [42]:

$$\alpha(h\nu)=A(h\nu-E_g)^{1/2} \quad (1)$$

Where α is the absorption coefficient and E_g is energy band gap of the semiconductor, respectively. According to Eq (1), plots of $(\alpha h\nu)^2$ versus energy ($h\nu$) for ZnWO₄ (pH 9) were shown in **Fig. 6**. From the tangent line of the curve, E_g of ZnWO₄ was calculated as 3.70eV. The E_g of all samples were tabulated in **Table 1**.

Table 1 E_g of ZnWO₄ synthesized in different pH value

Sample	pH 4	pH 6	pH 9	pH 12
E_g	3.25	3.61	3.70	3.62

The valence band potentials of ZnWO₄ can be calculated by the empirical equation [43]:

$$E_{VB} = X - E_c + 0.5E_g \quad (2)$$

where E_{VB} is the valence band edge potential, X is the electronegativity. Its can be calculated by the geometric mean of the electronegativity, $X=(X(A)^aX(B)^bX(C)^c)^{1/(a+b+c)}$. The electronegativity of atom for ZnWO₄ was tabulated in **Table 2**, based on the calculation, the X value is 6.31eV. E_c is about 4.5eV which is the energy of free electrons on a hydrogen atom. In addition, the conduction band position was calculated by $E_{CB}= E_{VB} - E_g$. The E_g of ZnWO₄ was calculated as 3.70eV according to **Fig.6**. Herein, the conduction band and valence band edge potentials of ZnWO₄ were -0.04 and +3.66eV, respectively.

These results show the photogenerated holes of ZnWO₄ can react with OH⁻ to generate ·OH due to their valence band edge is more positive than OH⁻/·OH couple [7]. Hydroxyl radical has the advantages of strong oxidation, strong deactivation effect on oceanic microorganisms, and no second pollution for oceanic environment.

Fig. 6 UV-vis DRS spectra of ZnWO_4 and plots of $(\alpha h\nu)^2$ versus energy ($h\nu$)

Table 2 the electronegativity of atom for ZnWO_4

Atom	Zn	W	O
X	4.45	4.40	7.54

Table 3 BET surface area of ZnWO_4

Sample	pH 4	pH 6	pH 9	pH 12
BET surface area (m^2/g)	27.972	24.327	17.976	11.169

The specific area of ZnWO_4 obtained at different pH value was demonstrated by the analysis of N_2 adsorption-desorption. Then the results calculated by the Brunauer Emmett Teller (BET) model. The BET specific ares (S_{BET}) of all samples were summarized in **Table 3**, with the increase of pH, the S_{BET} of ZnWO_4 decreased.

FT-IR analyses of ZnWO_4 were performed to examine the hydrogen-related defects (**Fig. 7**). Defects act as center of recombination for photogenerated electrons and holes, which will lead to the photocatalytic activity declined. The peaks at 473 and 834 cm^{-1} can be ascribed to Zn-O and Zn-O-W. The peaks at 633 and 710 cm^{-1} were assigned to W-O. The peaks at 1620 cm^{-1} can be ascribed to basic hydroxyl groups, which imply that there were some hydroxyl groups on ZnWO_4 surface. In the synthesis process, theses surface hydroxyl groups will lead to forming hydrogen-related defects. The peaks at 1385 cm^{-1} can be attributed to hydrogen-related defects [44] which decreased with pH value increased. According to the EIS experiment, we know the separation efficiency of the electron-hole pairs increase first and then decrease with increase of pH value (**Fig. 1 (c)-(d)**). Despite decreased defect,

the specific surface areas became smaller significantly, which restrict its photocatalytic and photoelectrocatalytic activities.

Thus, one may conclude that, according to the FT-IR and BET data, there is an appropriate ratio between BET surface and hydrogen-related defects.

Fig. 7 FT-IR spectra of ZnWO₄ prepared at different pH values

With further analysis the explanation is based on the first principles calculation. All the calculations were performed by the CASTEP package. For calculation of the electronic density of states (DOS), we used a plane wave cutoff energy of 340eV and 5×4×5 k-point for ZnWO₄, 340eV and 5×2×5 k-point for (0 1 0) and (0 1 1) surface of ZnWO₄.

Fig. 8 (a) shows the band structure and density of states (DOS) of ZnWO₄. Based on the calculations, the valence band position was occupied by O_{2p}, and the conduction band was occupied by W_{5d} and O_{2p}. The photogenerated electrons from O_{2p} to W_{5d} when ZnWO₄ film electrodes are under UV light irradiation.

According to HRTEM results the ZnWO₄ exposed (0 1 0) facets under weakly acid conditions, and exposed (0 1 1) facets under alkaline conditions. The ZnWO₄ (0 1 0) and (0 1 1) surfaces were shown in **Fig. 8 (b)**; the O atoms are in red, W in blue and Zn in violet. As we can see, both (0 1 0) and (0 1 1) exposed the O atom, which indicates that ·OH can be easily formed on the (0 1 0) and (0 1 1) facets. What is different is atom density in different surfaces, which will lead to different surface energy.

In order to compare the adsorption capacity of OH⁻ on (0 1 0) and (0 1 1) surfaces,

their surface energies ($E_{\text{surf.}}$) were calculated. The surface energy, which depends on the conservation of energy, is calculated as follows:

$$E_{\text{total}} = E_{\text{atoms}} + 2E_{\text{surf.}} \quad (3)$$

$$E_{\text{atomsp}} = nE_{\text{atoms}} \quad (4)$$

$$E_{\text{surf.}} = (E_{\text{total}} - E_{\text{atomsp}}/n)/2 \quad (5)$$

E_{total} is the total energy of ZnWO_4 surface. E_{atoms} is the total energy of ZnWO_4 surface. E_{atomsp} is the energy of the perfect unit cell; n is the supercell number in perfect unit cell. There are two surfaces on the supercells of the exposed (0 1 0) and (0 1 1) surface because of periodicity of the first principles. According to the surface energy calculations, $E_{\text{surf.}(0\ 1\ 0)} < E_{\text{surf.}(0\ 1\ 1)}$, which means (0 1 1) surfaces are more unstable than (0 1 0) surfaces. In the liquid phase reaction, the adsorption effect of H^+ and OH^- were affected by the pH value. The adsorption equilibrium in the water is written as:

The catalyst surface can absorb more H^+ in acid solution, OH^- in alkaline solution. Generally, the pH value of seawater is 7.5-8.3, so the ZnWO_4 film electrodes surface will absorb more OH^- in seawater.

Therefore, on the basis of minimum surface energy, OH^- adsorption in (0 1 1) surfaces are higher than (0 1 0) surface, so the hydroxyl radical preferred forming on (0 1 1) surface. For our best knowledge, the hydroxyl radical ($\cdot\text{OH}$) has strong oxidation ability, which can break down proteins and destroys DNA [45]. Based on our work, more hydroxyl radicals produced by photocatalysis and photoelectrocatalysis of ZnWO_4 film, and the exposure of (0 1 1) facets displayed a stronger deactivation microorganisms (chlorella) performance.

Fig.8 (a) Density of states (DOS) for ZnWO₄; (b) (0 1 0) and (0 1 1) surface of ZnWO₄; (c) photoelectrocatalytic deactivation mechanism of microorganisms by the ZnWO₄ film electrodes

The schematic of ZnWO₄ film electrode deactivation the microorganisms were shown in **Fig. 8(c)**. When the ZnWO₄ film electrode is under UV light irradiation, photogenerated electron-hole pairs were produced on the film surfaces. Then, the holes will capture OH⁻ to form ·OH.

At the same time, the photocatalytic activities will be enhanced by the external bias. When the voltage was applied to the ZnWO₄ film electrodes, the electrons would be transferred to the Ti electrode effectually under UV irradiation. The deactivation efficiency will be greatly improved because the recombination efficiency of the photogenerated electrons and holes greatly declined. In this reaction, ZnWO₄ film electrodes with (0 1 1) facets exposed showed enhanced activities by photoelectrocatalytic methods. Therefore, combining the two approaches can be a very effective way to deactivated microorganisms in ballast water.

Conclusion

Different crystal faces of ZnWO_4 were exposed by adjusting the pH value. Then ZnWO_4 was made into film electrodes via a coating method, which were applied in photocatalytic and photoelectrocatalytic deactivation of microorganisms (chlorella) in ballast water. The ZnWO_4 film electrodes exposure of (0 1 1) facets exhibited the best photocatalytic and photoelectrocatalytic activities. Based on experimental data and the first principles calculation, we believe that appropriate facets exposed and bias potential can boost the separation efficiency of hole and electron pairs which co-enhance the activity of ZnWO_4 film electrodes. This work provides the way to reduce the environmental hazards brought by ballast water letting directly via photocatalysts films.

Acknowledgments

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