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https://doi.org/10.1007/s11426-019-9672-8

A visible-light-photocatalytic water-splitting strategy for sustainable hydrogenation/deuteration of aryl chlorides

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Received November 26, 2019; accepted December 24, 2019; published online February 17, 2020

Hydrogenation/deuteration of carbon chloride (C–Cl) bonds is of high significance but remains a remarkable challenge in synthetic chemistry, especially using safe and inexpensive hydrogen donors. In this article, a visible-light-photocatalytic water-splitting hydrogenation technology (WSHT) is proposed to *in-situ* generate active H-species (i.e., H_{ad}) for controllable hydrogenation of aryl chlorides instead of using flammable H₂. When applying heavy water-splitting systems, we could selectively install deuterium at the C–Cl position of aryl chlorides under mild conditions for the sustainable synthesis of high-valued added deuterated chemicals. Sub-micrometer Pd nanosheets (Pd NSs) decorated crystallined polymeric carbon nitrides (CPCN) is developed as the bifunctional photocatalyst, whereas Pd NSs not only serve as a cocatalyst of CPCN to generate and stabilize H (D)-species but also play a significant role in the sequential activation and hydrogenation/deuteration of C–Cl bonds. This article highlights a photocatalytic-WSHT for controllable hydrogenation/deuteration of low-cost aryl chlorides, providing a promising way for the photosynthesis of high-valued added chemicals instead of the hydrogen evolution.

deuteration, water-splitting, aryl chlorides, Pd nanosheets, carbon nitride

Citation: Ling X, Xu Y, Wu S, Liu M, Yang P, Qiu C, Zhang G, Zhou H, Su C. A visible-light-photocatalytic water-splitting strategy for sustainable hydrogenation/deuteration of aryl chlorides. *Sci China Chem*, 2020, 63, https://doi.org/10.1007/s11426-019-9672-8

1 Introduction

Carbon chloride bonds widely exist in natural products and various significant organic compounds [1]. Activation of C–Cl bonds has attracted significant interest due to the inherent fundamental challenge [2]. Conventional dechlorination strategies mainly include metal halogen exchange, metal hydride reagents, or radical-induced reduction with organic

donors (amines, alcohols, and Hantzsch ester) as hydrogen transfer reagents [1-13]. These processes suffer from the undesired side reactions, the limited reaction scopes and the risks involved using flammable gas at high pressure, or operating air and moisture-sensitive metal hydride reducing agents. Consequently, it is an urgent to develop sustainable processes for the dechlorination of chlorides with low-cost and readily available hydrogen donors. Being clean and abundant, water is an ideal hydrogen donor. Moreover, the processes using aqueous chemistry are preferred due to re-

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duced likelihood of side reactions and simplified work-up procedures [14,15].

Although using hydrogen generated from water [16-18] is extremely attractive from the view of sustainable development. the activation of water molecules to generate hydrogen is challenging due to the high dissociation energy of O-H bonds [19]. Most recently, our group has demonstrated a photocatalytic water splitting technology [20-24] for hydrogenation (deuteration) reactions of iodides and carboncarbon multibonds [23,24]. Compared with iodides, chlorides are much lower-cost and exist in a larger number of natural products and pharmaceutically important molecules. Thus, the development of an environmental benign strategy for effective hydrogenation/deuteration of more inert carbonchloride bonds with sustainable H-donors (i.e., water) is highly attractive but still remains challenges for producing high-value-added fine chemicals as well as heavy drugs, which is currently a significantly important topic in pharmaceutical fields [25-30].

In this article, we demonstrated an efficient and sustainable visible light-induced C–Cl activation for hydrogenation/ deuteration of aryl/heteroaryl chlorides based on the photocatalytic water-splitting hydrogenation technology (WSHT) over submicrometer Pd nanosheets decorated by the crystalline polymeric carbon nitrides (denoted as Pd NSs/ CPCN). A series of aryl/heteroaryl chlorides were effectively hydrogenated/deuterated in aqueous solution under mild conditions (room temperature, ambient tolerance). The ultrathin Pd NSs as the cocatalyst employed herein not only promote the hydrogen generation and stabilization, but also play a critical role in the activation of C–Cl bonds.

2 Experimental

2.1 General information

Common reagents were commercially available and used as received without any further purification unless stated otherwise. Pd(acac)₂, melamine and KBr were purchased from commercial sources (Sigma-Aldrich and Alfa Aesar, USA) and used as received. Transmission electron microscope (TEM) images were taken using a Tecnai F30 (FEI) and Titan Cubed Themis G2 300 (FEI). X-ray diffraction (XRD) patterns were performed on Rigaku Ultima IV using Cu K α irradiation at a scan rate of 2° min⁻¹ with the target voltage of 40 kV and the current of 40 mA. The UV-Vis absorption spectra were recorded on a UV-3600 UV-Vis-NIR scanning spectrophotometer (Carry 5000, Agilent, USA). The chemical compositions were analyzed using X-ray photoelectron spectroscopy (XPS, Thermo Escalab 250, USA, a monochromatic Al Ka X-ray source. All binding energies were referenced to the C 1s peak (284.6 eV) arising from adventitious carbon). The content of palladium was measured by inductively coupled plasma-optical emission spectrometry (ICP-OES, Agilent 700). The high-performance mass spectrometry (MS) was conducted by a Q Exactive GC Orbitrap GC-MS/MS (Thermo Scientific). Nuclear magnetic resonance (NMR) spectra were recorded on Bruker Nanobay spectrometers 500, 600 MHz (Germany). In CDCl₃, proton chemical shifts (δ) are reported relative to the residual protonated solvent (δ =7.26 ppm). The photocatalytic reaction systems were irradiated by Kessil LED lights (PR160–427 nm).

2.2 Preparation of Pd NSs

Pd(acac)₂ (50 mg) was added into a glass-pressure vessel with oleyamine (8 mL) and *N*,*N*-dimethylformamide (DMF) (2 mL). The vessel then was purged with 1 atm CO and heated at 90 °C for 3 h. After being cooled to room temperature, the obtained products was precipitated with acetone, centrifuged and further washed with ethanol for twice. The precipitate was re-dispersed into DMF (40 mL) for the further use.

2.3 Preparation of CPCN

According to the typical procedure [31], melamine (3.0 g) was ground with KBr (2.0 g) in 3 mL EtOH and 1 mL glycol in an agate mortar. After drying at 65 °C, the resultant mixture was heated to 550 °C for 3 h at a rate of 3.3 °C min^{-1} in a tube furnace (inner diameter is 5 cm) with open two ends in an air atmosphere. After it was cooled to room temperature, the bright yellow green product was washed with boiling deionized water several times and collected by filtration, followed by drying at 60 °C under vacuum.

2.4 Synthesis of Pd NSs/CPCN

226 mg CPCN and 100 mL DMF was stirred overnight and then sonicated for 1 h. The Pd NSs in 40 mL DMF described above were added into the dispersion and stirred for about 12 h. Finally, the mixture was centrifuged and washed with ethanol for twice and dried under vacuum. By varying the amount of CPCN, Pd NSs/CPCN with different Pd contents was prepared.

2.5 Photocatalytic H₂ evolution

The photocatalytic water splitting was carried out in a 150 mL Pyrex flask reactor (Labsolar VIAG, Perfectlight Technology Co., Ltd., China) via top-irradiation with a 300 W xenon lamp (Perfect Light Company Solaredge 300C) with a UVCUT-420 nm filter (Newport). The temperature of the reaction system (10 °C) was controlled by the circulated water. Typically, the PdNSs/CPCN photocatalyst

(20 mg) was suspended in an aqueous solution containing 10 vol% triethanolamine (TEOA) solution. The evolved gas was quantified online using a gas chromatograph (GC, Fuli 9890II, China) equipped with a thermal conductivity detector (TCD) with argon as the carrier gas.

2.6 Apparent quantum yield (AQY) calculations of H₂ production

The 100 mg of Pd NSs/CPCN photocatalyst is placed into a 100 mL pure water in a closed gas circulation system. The catalyst solution was irradiated by a 300 W Xe lamp applying band pass filters (centered at 400, 420, 475, 500 and 550 nm) for 2 h. The average intensity of irradiation is determined by a FZ-A spectroradiometer (Photoelectric Instrument Factory of Beijing Normal University).

The AQY was calculated from the equation:

$$AQY = \frac{2 \times \text{the number of evolved } H_2 \text{ molecules}}{\text{the number of incident photos}} \times 100\%$$

2.7 General procedure of photocatalytic reactions

A silica tube containing the catalyst, substrate (0.2 mmol), TEOA (0.9 mL), H₂O (8.1 mL) and ethanol (1 mL), was sealed in a glovebox and transferred outside. Then the mixture was irradiated under the LED light (427 nm) with stirring for 24 h. Ether acetate (5 mL) was added to the mixture and the upper organic phase was collected. The yield was calculated by GC-MS with the standard curve and by NMR. For photocatalytic stability evaluation, the catalyst was re-collected by centrifugation, washed with ethanol and dried under vacuum. For deuteration, D₂O and CH₂CH₂OD were used instead of water and ethanol.

3 Results and discussion

To synthesize sub-micrometer Pd NSs, Pd(acac)₂ was dissolved in DMF and reduced by CO in the presence of olevamine at 90 °C for 3 h. The color of the reaction mixture turned to blue-black from the initial light vellow as the reaction progressed. After being cooled to room temperature, the mixture was precipitated with acetone and centrifuged. The obtained Pd NSs were washed twice with ethanol and redispersed in DMF for further use. The TEM image in Figure 1(a) reveals that the as-prepared Pd NSs are hexagonal morphology with a size of over 100 nm (the long diagonal of the hexagon). The high-resolution TEM (HRTEM) image of the individual Pd nanosheet (Figure 1(b)) exhibits the lattice fringes with an interplanar spacing of 0.24 nm, corresponding to 1/3(422) fringes of face centered cubic (fcc) Pd [32]. The fcc structure of Pd NSs was further determined by X-ray diffraction (XRD) pattern (Figure 2(a)). The result indicates that the (111) facet of Pd NSs is the basal planes, which is consistent with the previous reports [32,33].

The Pd NSs/CPCN nanocomposite was constructed via the electrostatic adsorption in DMF through stirring Pd NSs described above and CPCN for over 12 h. After being homogeneously mixed, the color of Pd NSs/CPCN dispersion changed from yellow (CPCN) to dark blue, and the composite was obtained after centrifugation and drying. Three Pd NSs/CPCN catalysts with different contents of Pd were prepared by varying the amount of CPCN, named as Pd NSs/CPCN-1, Pd NSs/CPCN-2 and Pd NSs/CPCN-3, respectively. The color of the three resulting Pd NSs/CPCN nanohybrids is deepening to blackish green, as shown in Figure S1 (Supporting Information online). The contents of Pd of Pd NSs/CPCN-1, Pd NSs/CPCN-2 and Pd NSs/CPCN-3 were measured to be approximately 1.9%, 5.8% and 9.1%



Figure 1 (a, b) TEM and HRTEM images of Pd NSs. The inset in (b) is the FFT pattern from the marked yellow square. (c) TEM image of Pd NSs/CPCN-2. (d) The HAADF-STEM image and element mapping patterns of Pd NSs/CPCN-2 (color online).



Figure 2 (a) XRD patterns of Pd NSs, CPCN and Pd NSs/CPCN-2. (b) UV-Vis-NIR diffuse reflectance spectra of CPCN and Pd NSs/CPCN-2 (color online).

(Table S1, Supporting Information online) by ICP-OES, respectively. As illustrated in Figure 2(a), the slightly decreased peak intensity of Pd NSs/CPCN-2 could be ascribed to the interaction between Pd NSs and CPCN in Pd NSs/ CPCN-2, which might be beneficial to improve the photocatalytic activity. The light absorption edge shows negligible difference of Pd NSs/CPCN-2 compared with CPCN in the UV-Vis-NIR diffuse reflectance spectra (Figure 2(b)) ranging from 300 to 500 nm. The increased absorption of Pd NSs/CPCN-2 in the range of 500 to 1,200 nm is attributed to the intrinsic absorption of Pd NSs. To observe the structure of Pd NSs/CPCN and the distribution of Pd NSs in Pd NSs/ CPCN, the spherical aberration-corrected scanning transmission electron microscopy in high angle annular dark field mode (C_s-corrected STEM-HAADF) was conducted on the sample Pd NSs/CPCN-2. As shown in Figure 1(c, d), Pd NSs were dispersed rather well on the surface of CPCN. The energy-dispersive X-ray spectroscopy (EDS) elemental mapping images (Figure 1(e-h)) further confirmed the good dispersion of Pd NSs on surface of CPCN. XRD was further employed to characterize the crystal structure of Pd NSs/ CPCN-2. In Figure 2(a), the decorated Pd NSs only reduce the peak intensity of CPCN.

The chemical states of Pd NSs, CPCN and Pd NSs/CPCN

were evaluated through XPS spectra. As shown in Figure 3 (a), the peaks at 336 and 341.2 eV in Pd NSs are assigned to Pd 3d_{5/2} and Pd 3d_{3/2} of Pd(0), respectively. However, the binding energy of Pd 3d in Pd NSs/CPCN exhibits an obvious decrease of 0.5 eV compared with Pd NSs. Correspondingly, the binding energy of N 1s in Pd NSs/CPCN-2 displays 0.4 eV increase compared with the pure CPCN (Figure 3(b)). This result indicates that the strong metalsupport interaction (SMSI) [34,35] appears at the interfaces between Pd NSs and CPCN. This might be due to the in-built amino groups in the CPCN skeleton that could act as the binding sites to interact with Pd NSs. Accordingly, the electron cloud density surrounding the interface between Pd NSs and CPCN increases. This would finally affect the catalytic performance of the Pd NSs/CPCN.

The photocatalytic water splitting is a process of decomposing the O–H bonds of water, resulting in the generation of active H-species (H_{ad}) which subsequently form hydrogen molecules. Hence, the H₂ production activity of Pd NSs/ CPCN-2 was evaluated by carrying out the visible lightinduced hydrogen evolution assay on the Pd NSs/CPCN-2. As shown in Figure 4(a), Pd NSs/CPCN exhibits an excellent photocatalytic activity. The hydrogen evolution rate of Pd NSs/CPCN reaches up to 2.53 mmol $h^{-1} g^{-1}$ with a quantum



Figure 3 Pd 3d (a) and N 1s (b) XPS spectrum of Pd NSs and Pd NSs/CPCN-2 (color online).



Figure 4 (a) Photocatalytic H₂ evolution over Pd NSs/CPCN-2 and Pd NSs/CPCN-2 after three cycles of hydrogenated dichlorination process under visible light ($\lambda \ge 420$ nm). (b) Photocatalytic stability of Pd Ns/CPCN-2 towards hydrogenation of 2-chloro-benzonitrile (color online).

efficiency of approximate 2.4% in the initial hour. By replacing water with heavy water, the active D-species could be obtained by this technology for the further deuteration. The H₂ evolution result indicates that Pd NSs/CPCN might be able to achieve the aim by using the *in-situ* generated active D-species as D donors for the subsequent deuteration of inert aryl chlorides. In this proposed process, Pd not only serves as cocatalysts for heavy water splitting to generate and stabilize D-species, but also plays a major role in the sequential activation and deuteration of C–Cl bonds. The high atom utilization ratio and specific surface area of Pd NSs employed in the Pd NSs/CPCN could enlarge the contact area between Pd and CPCN to enhance the electron transfer on the interface as well as increase the adsorption ability of the photogenerated active D-species and chloride substrates.

Since the core of our strategy described above is utilizing the in-situ generated active D (H) species to achieve the deuterium (hydrogen) incorporation in the aryl/heteroaryl ring via the C-Cl bond cleavage, we chose the hydrogenated dechlorination of inert aryl chlorides as the initial model reaction to study the transformation of C-Cl bonds. As shown in Table S2, a series of control experiments were carried out with 2-chloro-benzonitrile as the model substrate to optimize reaction conditions and confirm the synergistic effect of Pd NSs/CPCN during the hydrogenated dichlorination process. First, in the case of only pure water in the system with Pd NSs/CPCN-2 (40 mg) as the catalyst (entry 1) under blue light irradiation (427 nm) for 24 h, only trace amount of the product was detected by the GC-MS. In Table S2 entry 2, the yield increased dramatically to 94.2% when TEOA used as a sacrificial agent was added into the system. The highest yield was obtained because the hydrophilic solvent ethanol was used to enhance the solubility of substrates in water (Table S2, entry 3). Hence, the TEOA/ H₂O/ethanol system was determined to be the optimal reaction system. Then catalytic performances of various catalysts (Pd NSs/CPCN-1, Pd NSs/CPCN-2 and Pd NSs/CPCNwith different Pd amounts were evaluated with the TEOA/ H₂O/ethanol system shown in Table S2 entry 4–6. From the obtained results, Pd NSs/CPCN with a Pd content of 5.8% (Pd NSs/CPCN-3) are chosen as the optimal catalyst. Moreover, no reaction occurs under all conditions (Table S2 entry 7-9) except for using Pd NSs/CPCN as a photocatalyst under blue light irradiations. This indicates that both the light and the synergistic photocatalyst are essential for the hydrogenated dechlorination reaction. Moreover, the effect of irradiation sources with different wavelength (λ =510 and 610 nm) was also estimated. As shown in Table S1 entry 10 and 11, the yield of the hydrogenation/deuteration of chlorides decreased dramatically when increasing the wavelength of the LED lamp. This indicated that H₂/D₂ evolution efficacy decreased when increasing the wavelength, resulting in the reduction of the reaction efficiency of the following hydrogenated dichlorination/deuteration. Subsequently, the photocatalytic stability of Pd NSs/CPCN was examined with catalytic Pd NSs/CPCN-2. As shown in Figure 4(b), Pd NSs/ CPCN maintained the excellent activity during the first two cycles. However, the catalytic ability of Pd NSs/CPCN-2 decreased to 80.9% in the third cycle and further to 61.7% in the fourth cycle. Moreover, the photocatalytic H₂ evolution performances over Pd NSs/CPCN-2 after three cycle reaction decreased to around 50% (Figure 4(a)). Therefore, it indicated that the decreased hydrogenation/deuteration ability of Pd NSs/CPCN could be ascribed to the reduced photocatalytic H₂ evolution performance. To further confirm this, the Pd NSs/CPCN-2 after three cycles was used to perform the control experiment, where the hydrogenated dichlorination of 2-chloro-benzonitrile was conducted in the TEOA/H₂O/ethanol system with the hydrogen gas (1 atm) but without the light irradiation. The 2-chloro-benzonitrile was fully converted to the corresponding product at room temperature as shown in Table S2 entry 12, which further confirmed that the decreased hydrogenation/deuteration ability of Pd NSs/CPCN could be attributed to the reduced photocatalytic H₂ evolution performance.

Under the optimal condition, a variety of aryl/heteroaryl chlorides and two drug chlorides were examined to assess the universality of photocatalytic hydrogenated dechlorination of chlorides with water as the hydrogen source. In Table 1, the electron-withdrawing group-substituted aryl chlorides such as cyano or carbonyl groups in various positions (2a-2c and 2e-2h) efficiently gave the desired hydrogenated products with high yields through the TEOA/H2O/ethanol system. Even the electron-donating group-substituted aryl chlorides such as m- or p-chloro-benzamine (2m and 2n) and chloro-naphthene (2d) are suitable for this strategy. However, the TEOA/H₂O/ethanol system was not suitable for aryl chlorides containing the ester groups. When replacing TEOA/H₂O/ethanol with MeOH/H₂O, aryl chlorides (2i–2l), containing the ester groups, could gave the aim products with excellent yields. The C-F bond cannot be hydrogenated in this system due to the much higher bond energy. Furthermore, the heteroaryl chlorides (20-2v) and two bioactive chlorides (2w and 2x) were also appropriate for our strategy in the TEOA/H2O/ethanol system, generating the corresponding hydrogenated products with remarkable yields.

Based on the optimal conditions of hydrogenated dechlorination, replacing water and ethanol with D_2O as the D source and CH_3CH_2OD as solvent, respectively, the reaction scope towards the deuteration of aryl/heteroaryl chlorides was assessed, where TEOA without the D-label was still used as the sacrificial agent. As illustrated in Table 2, the deuteration occurs at the position of C–Cl bonds of aryl/heteroaryl chlorides in high yields with good to excellent deuterium incorporation. Additionally, the functional group tolerance of our strategy is rather good. However, for **30**, using 6-chloroquinoline as the substrate, deuteration occurs





a) Chloride substrate (0.2 mmol), TEOA/H₂O/ethanol (0.9 mL/8.1 mL/ 1.0 mL), Pd NSs/CPCN-2 (40 mg), irradiation 24 h. Yields were calculated from GC-MS measurements using a standard curve. b) Methanol/H₂O (5.0 mL/5.0 mL). c) Irradiation 48 h.

 Table 2
 Deuteration of aryl/heteroaryl chlorides^{a)}



a) Chloride substrate (0.2 mmol), TEOA/D₂O/CH₃CH₂OD (0.9 mL/8.1 mL/1.0 mL), Pd NSs/CPCN-2 (40 mg), irradiation 24 h. b) CD₃OD/D₂O (5.0 mL/5.0 mL). Yields were calculated from GC-MS measurements using a standard curve.

not only at the position of C–Cl bonds (86% D incorporated) but also at the α active hydrogen of quinoline (95% D incorporated). It indicated that when the chloride substrate possesses active hydrogens, the hydrogen isotope exchange will take place in the process of chloride deuteration. Thus, 2-chloroquinolin was further used as the substrate, where the α active position was substituted by the chlorine. Deuteration only occurs at the position of C–Cl bonds with good deuterium incorporation (85%). In general, our strategy is able to efficiently transform C–Cl bonds of aryl/heteroaryl and bioactive chlorides to C–D bonds in good deuterium incorporation with green and low-cost D-sources under mild conditions.

Accordingly, based on the obtained experimental results described above, a possible mechanism of the photocatalytic C–Cl bonds by hydrogenated dechlorination/deuteration was proposed (Figure 5). First, the inert chlorides are adsorbed on the surface of Pd NSs and activated by Pd NSs [36]. Upon the blue light LED irradiation, the excited electrons in CPCN will transfer to Pd NSs [37,38]. Subsequently, the electrons will reduce H₂O (D₂O) to H₂ (D₂), which further adsorbs on the surface of Pd NSs. Then, Pd NSs catalyze the hydrogenated dichlorination/deuteration of C–Cl bonds by use of the generated H₂ (D₂). Meanwhile, the generated holes can oxidize TEOA to [TEOA]⁺ [39].

4 Conclusions

In conclusion, the efficient and selective transformation of C–Cl to C–H has been achieved with *in-situ* generated hydrogen active species from aqueous solution under visible light over Pd NSs decorated CPCN. A variety of aryl and heteroaryl chlorides were effectively hydrogenated under mild conditions in remarkable yields with good functional group tolerance. By replacing H₂O with D₂O, the *in-situ*



Figure 5 The proposed mechanism of the photocatalytic hydrogenation/ deuteration reaction (color online).

generated active D-species were utilized for the visible light photocatalytic deuteration of inert C–Cl bonds to produce high-value-added D-chemicals. This work highlights a sustainable strategy utilizing aqueous solutions as the H (D)source for the sustainable hydrogenation/deuteration of inert chlorides, opening the possibility for the efficient and sustainable production/innovation of new heavy drugs with improved pharmacokinetic and toxicity profiles. Further applications of WSHT for converting a series of functionalities, such as C–H, C–OH, C=O, to C–D bonds are currently ongoing for the controllable synthesis of heavy chemicals/drugs.

Acknowledgements This work was supported by the National Natural Science Foundation of China (21972094, 51701127, 21401190), China Postdoctoral Science Foundation (2017M612709), Guangdong Special Support Program, Pengcheng Scholar Program, Shenzhen Peacock Plan (KQJSCX20170727100802505, KQTD2016053112042971), Educational Commission of Guangdong Province (2016KTSCX126), Foundation for Distinguished Young Talents in Higher Education of Guangdong (2018KQNCX221), Shenzhen Innovation Program (ICYI 20170818142642395). We are thankful for the support of TEM characterizations from the Electron Microscopy Center of Shenzhen University and computational source supplied by the National Supercomputing Center in Shenzhen (Shenzhen Cloud Computing Center).

Conflict of interest The authors declare that they have no conflict of interest.

Supporting information The supporting information is available online at http://chem.scichina.com and http://link.springer.com/journal/11426. The supporting materials are published as submitted, without typesetting or editing. The responsibility for scientific accuracy and content remains entirely with the authors.

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