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# Making g-C<sub>3</sub>N<sub>4</sub> ultra-thin nanosheets active for photocatalytic overall water splitting



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#### ABSTRACT

The photocatalytic solar water splitting with Pt loaded graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) and without sacrificial reagent is still a big challenge. In this work, g-C<sub>3</sub>N<sub>4</sub> nanosheets were exfoliated for the first time by a femto-second pulsed laser. After loaded with 1.4 wt.% of Pt, g-C<sub>3</sub>N<sub>4</sub> becomes active towards the overall water splitting with a production rate of 42.6 µmol/g/h for H<sub>2</sub> and 18.7 µmol/g/h for O<sub>2</sub> (H<sub>2</sub>/O<sub>2</sub> = 2.28). Compared to inactive ultrathin g-C<sub>3</sub>N<sub>4</sub> nanosheets from conventional exfoliation, our experiments and density functional theory (DFT) calculations revealed that the cyano (-C=N) defects created by laser pulses favor the anchoring of Pt atoms. These divalent atomic Pt cocatalysts, distinct from Pt metal nanoparticles, not only provide more active sites for the surface reaction but also largely suppress the backward reaction of water splitting. In addition, the -C=N defects shift down the band edge positions, thus enhancing the oxidizing power of holes.

### 1. Introduction

Photocatalytic overall water splitting into H<sub>2</sub> and O<sub>2</sub> is a promising way to convert solar energy into renewable fuels [1,2]. Numerous semiconductors have been developed in last decades [2–5], among them two-dimensional (2D) metal-free g-C<sub>3</sub>N<sub>4</sub> has attracted great attention due to its good stability, relatively narrow bandgap ( $\sim 2.7 \text{ eV}$ ), and suitable band edge positions (*i.e.* conduction band minimun of -0.5  $\sim$  -1.5 eV vs. NHE and valence band maximun of 1.3  $\sim$  2.0 eV vs. NHE) [6–14]. Despite its perfect thermodynamic driving forces for both the hydrogen evolution (HER) and oxygen evolution reactions (OER), g-C<sub>3</sub>N<sub>4</sub> alone can hardly perform the overall water spliting due its poor intrinsic activity. The current strategies to solve these problems are decorating cocatalysts for both HER and OER reactions [15–17] or designing heterojunctions to facilitate the charge separation [18–24]. For example, an oxygen evolution cocatalyst (*e.g.*  $Co_3O_4$ ,  $IrO_2$  or CoP) and a hydrogen evolution cocatalyst (*e.g.* Pt) are typically co-loaded onto g- $C_3N_4$  photocatalyst to lower their overpotentials and to spatially separate the water reduction and oxidation reactions [15–17]. Heterojunctions in both atomic and nano-scales have been prepared, respectively, by incorporating graphene (*i.e.* carbon rings) into g- $C_3N_4$  structure [22,24] and by integrating g- $C_3N_4$  with an OER photocatalyst (*i.e.* semiconductors like MnO<sub>2</sub> [18], Fe<sub>2</sub>O<sub>3</sub> [20,23], BiVO<sub>4</sub> [23] and WO<sub>3</sub> [21,23] that have deep valence bands).

As a simpler system,  $g-C_3N_4$  loaded with Pt as the sole (HER) cocatalyst has been intensively studied in H<sub>2</sub> production half reaction (*i.e.* with sacrificial reagent) since 2008 [6–9] but has not achieved overall water splitting catalyst until the first report in 2016 by Zhang et al. [25] In that paper, the authors claimed that ultrathin 2D g-C<sub>3</sub>N<sub>4</sub> nanosheets (~ 2 nm) loaded with multi-valent Pt (*i.e.* Pt-PtO<sub>x</sub>) are crucial for

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achieving overall water splitting: the nanosheets reduced the diffussion path of electrons and holes to reach the surfaces while  $Pt-PtO_x$  acted as bifunctional cocatalysts for both HER and OER reactions. Despite its simple design and synthesis, there has been very few follow-up works in the past four years [15,26]. It is worth to note that  $Pt/g-C_3N_4$  catalysts with one-dimentional (1D) morphology (e.g. sea-urchin [27] and nanowire bundles [28]) have been reported by two different groups to split pure water. However, the complexity of their systheses of 1D morphology from the intrinsic 2D  $g-C_3N_4$  is hard to follow, and the unique property of 1D morphology is not clear yet.

Here we report a simple method to produce ultrathin nanosheets from bulk g-C<sub>3</sub>N<sub>4</sub> using a pulsed laser. Unlike nanosheets produced by conventional methods, the laser-exfoliated g-C<sub>3</sub>N<sub>4</sub> can split pure water into H<sub>2</sub> and O<sub>2</sub> when loaded with Pt cocatalyst. Fourier-transform infrared spectroscopy (FTIR), electron spin resonance (ESR), X-ray photoelectron spectroscopy (XPS), high-resolution transmission electron microscopy (HRTEM), High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), energy-dispersive X-ray spectroscopy (EDS) mapping as well as DFT calculations reveal that laser-exfoliated g-C<sub>3</sub>N<sub>4</sub> nanosheets become rich with  $-C \equiv N$  defects, which not only act as the anchoring site for Pt atoms but also lower the valence band edge. It is such Pt atoms and highly oxidative holes that make g-C<sub>3</sub>N<sub>4</sub> active for overall water splitting.

## 2. Results and discussion

The laser exfoliation was carried out by irradiating an aqueous suspension of  $g-C_3N_4$  with a femtosecond pulsed laser (150 fs) centered at 805 nm with an average power of 340 mW (setup shown in Fig. 1a) [29–32]. Images captured by a high-speed camera in the supporting materials (Figure S1) show that the laser pulses effectively break g-C<sub>3</sub>N<sub>4</sub> powders within 1–2 s with its generated strong shock waves [33].

According to X-ray diffraction (XRD) in Fig. 1b, the pristine g-C<sub>3</sub>N<sub>4</sub> (named CN0) exhibits two peaks at 13.1° and 27.4°, corresponding to the in-plane structural packing motifs (indexed as (100)) and the interlayer stacking of conjugated aromatic systems (indexed as (002)), respectively [34]. Both peaks became broader and weaker after the laser exfoliation, suggesting a decrease of size in both directions (*i.e.* parallel and vertical to the C<sub>3</sub>N<sub>4</sub> layers). As confirmed by atomic force microscopy (AFM) and transmission electron microscopy (TEM), the bulk g-C<sub>3</sub>N<sub>4</sub> (Fig. 1c and Fig. 2a) was completely transformed to lamellar structures with a size of tens nanometers and a thickness of ~ 2 nm after 3 h of laser exfoliation (Figs. 1d and 2 b, sample named CN180).

The CN0 and CN180 were tested in pure water after loading 1.5 wt. % of Pt though a photo-deposition process. As shown in Fig. 2, Pt/CN0 did not produce any  $H_2$  and  $O_2$  under the light irradiation (Fig. 2d), whereas Pt/CN180 showed a linear increase of both gases during the 9 h test (Fig. 2e). The reaction rates were 42.6 µmol/g/h for H<sub>2</sub> and 18.7  $\mu$ mol/g/h for O<sub>2</sub> (with a H<sub>2</sub>/O<sub>2</sub> ratio of 2.28), comparable to the sea-urchin [27] and nanowire bundle [28] shaped g-C<sub>3</sub>N<sub>4</sub> catalysts (Table S1). The apparent quantum efficiency is 0.23 % at 400 nm. The activity was also stable for at least 27 h (i.e. three cycles), and no evident changes occur on the material according to XRD, FTIR and STEM (Figure S2). Samples after 30 or 90 min. of laser exfoliation (named CN30 and CN90, respectively) were also tested, and the results showed that an insufficient laser exfoliation cannot make  $g-C_3N_4$  active for the overall water splitting (Figure S3). Considering that small thickness and large surface area can always facilitate the photoreaction on g-C<sub>3</sub>N<sub>4</sub>, an ultrathin g-C<sub>3</sub>N<sub>4</sub> (UTCN) was prepared as a reference through a thermal exfoliation [35] followed by an ultra-sonication assisted liquid exfoliation [36]. The obtained white UTCN nanosheets (Figs. 2c and S4) had a thickness  $(2 \sim 4 \text{ nm})$  comparable to the laser exfoliated nanosheets, while the diameter is relatively larger (a few micrometers).



Fig. 1. (a) The setup for femtosecond pulsed laser exfoliation and the evolution of the  $g-C_3N_4$  solution with time. (b) XRD patterns of CN0, CN90 and CN180. AFM images of (c) CN0 and (d) CN180.



Fig. 2. The TEM images of (a) CN0, (b) CN180 and (c) UTCN. CN0 was a mixture of particles with difference sizes. The inset in (a) was a bulk of  $\sim 1 \,\mu$ m. The photocatalytic overall water splitting of (d) CN0, (e) CN180 and (f) UTCN with  $\sim 1.4 \, \text{wt.\%}$  of Pt as cocatalyst.

Surprisingly, no  $H_2$  and  $O_2$  was produced at all in pure water (Fig. 2f), demonstrating that the reduced thickness is not the key reason for the overall water splitting.

To understand the activity of laser exfoliated g-C<sub>3</sub>N<sub>4</sub>, a series of techniques have been used to identify the difference of g-C<sub>3</sub>N<sub>4</sub> before and after the laser exfoliation. According to FTIR (Fig. 3a), the molecular structure of g-C<sub>3</sub>N<sub>4</sub> basically remained the same after laser exfoliation: the broad peak at  $3000 - 3500 \text{ cm}^{-1}$  is attributed to the N–H stretching mode; the strong bands from 1200 to 1775 cm<sup>-1</sup> are C–N and C=N stretching modes of the aromatic ring; while the sharp peak at  $808 \text{ cm}^{-1}$  is ascribed to the breathing mode of triazine units [37]. However, different from CN0 (Fig. 3a) and UTCN (Figure S4a), a new peak appeared at 2180 cm<sup>-1</sup> after the laser exfoliation, and the intensity increased with time. It was ascribed to the formation of  $\text{-}C\,{=}\,N$ groups, as a consequence of the opening of s-triazine units and the cleaving of C-N bonds [37-39]. These groups possibly appear at the edge sides or locate at less ordered C<sub>x</sub>N<sub>y</sub> minority domains [38]. The enrichment of structural defects by laser exfoliation was further confirmed by ESR analysis (Fig. 3b). The stronger magnetic signal at 3515 G in CN180 indicates a higher concentration of unpaired electrons, which generally come from the structural defects [40]. XPS was applied to identify the carbon and nitrogen species. As shown in Fig. 3c, there is no large change in the carbon species, including the sp2-bonded carbon of N-C=N (288.2 eV) and the adventitious carbon or sp2 C-C (284.8 eV) [37], except a slight increase of C-OH (286.1 eV) after the laser exfoliation [41]. In the case of nitrogen (Fig. 3d), the ratios of C-N=C (398.5 eV) to N-(C)<sub>3</sub> (400.1 eV) decreased from 5.2 to 2.0, while the ratio of N-H (401.2 eV) to N-(C)<sub>3</sub> decreased from 1.4 to 0.3, [42,43] further confirming the cleavage of the s-triazine units [37]. From the above results, the laser pulses with ultra-high peak power broke not only the weak van der Waals bonds between the C3N4 atomic layers but also the stronger C-N covalent bonds in the C3N4 layers, creating abundant  $-C \equiv N$  defects on the surface. In contrast, the conventional exfoliation only broke the interlayer van der Waals bonds.

 $-C \equiv N$  defects are certainly not directly related to the water splitting activity, so we investigated Pt cocatalysts on CN0 and CN180. As shown in TEM and HRTEM (Fig. 4a-c), CN0 presented a uniform distribution

of Pt NPs  $(3.2 \pm 0.7 \text{ nm})$  on the surface. The Pt NPs exhibited good crystallinity with the lattice spacing consistent with [100] facets of metallic Pt (Fig. 4c inset). Despite the similar Pt loadings on CN0 (1.37 wt.%) and CN180 (1.41 wt.%) according to inductively coupled plasma mass spectrometry (ICP-MS), CN180 displayed a "clean" surface that was free of Pt NPs (Fig. 4d). By zooming in the "clean" region under a HRTEM mode one can see a dispersion of round, isolated, and bright spots on an amorphous-like background (Fig. 4e). These spots were relatively brighter (heavy Pt atoms show bright contrast under overfocus conditions in the HRTEM mode [44]) and more uniform than those seen in g-C<sub>3</sub>N<sub>4</sub>, and their size ( $\sim 0.37$  nm) were close to the theoretical diameter of Pt atoms (i.e. 0.35 nm). HAADF-STEM in Fig. 4f further confirms atomic Pt and shows that they are uniformly dispersed over the dark g-C<sub>3</sub>N<sub>4</sub> substrate. EDS in Fig. 4g-j shows an even distribution of the Pt element on a C-N rich substrate with a low density. According to XPS in Figs. 4k and S6, nearly 64.8 % of the Pt in CN0 is in metallic state, while majority of the Pt (i.e. 84.4 %) in CN180 is positively charged (i.e. 2+). This is consistent with the reported metal atoms on g-C<sub>3</sub>N<sub>4</sub> or N doped carbon supports [45-49], in which the coordination of metal atoms with the neighboring nitrogen atoms and the subsequent charge transfer between them lead to a positive charge of the metal atoms [47,49].

To understand the relationship between  $-C \equiv N$  defects and atomic Pt, DFT calculation was carried out to compare the adsorption energy of Pt atoms on the original six-fold cavities (Fig. 41, usually regarded as the most stable sites for metal atoms in  $g-C_3N_4$  [45,47,50]) and the laser induced  $-C \equiv N$  defects (Fig. 4m). The former was calculated to be -2.58 eV, consistent with previous report [47], while the latter was almost the same (-2.56 eV). Therefore, these  $-C \equiv N$  defects provided additional stable sites for the accommodation of Pt atoms. This explains the relatively high loading of Pt atoms on the laser exfoliated CN180 (*i.e.* 1.41 wt.%), compared to the ones deposited on regular g-C<sub>3</sub>N<sub>4</sub> through the same photo-deposition method (*e.g.* up to 0.38 wt.%) [52].

To understand the activity of atomic Pt cocatalyst, we chose CN180 as the photocatalyst and gradually increased the Pt loading from 1 wt.%



Fig. 3. (a) FTIR spectra of CN0, CN90, and CN180. (b) Electron spin resonance (ESR) spectra of CN0 and CN180. (c) XPS-C 1s spectra of CN0, CN90, and CN180. (d) XPS-N 1s spectra of CN0, CN90, and CN180.

to 3 wt.% to transform the Pt atoms to clusters or NPs (samples named 1 Pt/CN180 ~ 3 Pt/CN180) [51]. In the presence of methanol (as hole scavenger), all the samples were active in H<sub>2</sub> production and increasing the Pt content resulted in a volcano-shaped trend of the activity (Fig. 5a). The increasing trend from 1 Pt to 1.5 Pt was due to the increase of Pt atoms as the active sites, while the decline by further adding Pt was caused by an aggregation of Pt atoms to clusters or NPs. This was proven by the high fraction of metallic Pt in 2.5 Pt/CN180 (with 43 % Pt°) and 3.0 Pt/CN180 (with 63 % Pt°) (Figure S7). However, in pure water, their activities are very different. The activity initially improved with the increase of Pt content from 0.5 to 2.0 wt.%, then it dropped dramatically to zero by further increasing the Pt content to 3.0 wt.% (Fig. 5a). It suggested that the aggregation of Pt atoms resulted in deactivation.

We believe that the apparent loss of water splitting activity of Pt NPs is due to their activity for water backward reaction. In fact, the backward reaction, *i.e.* oxygen reduction reaction (ORR), is thermodynamically available at room temperature and is widely applied in the proton exchange membrane fuel cell (PEMFC) to convert chemical energy into electrical energy [53–55]. To verify this possibility, the back-oxidation of H<sub>2</sub> over different Pt cocatalysts was evaluated by mixing a certain amount of H<sub>2</sub> with air in dark (Fig. 5b). In the presence of 1.5 Pt/CN180, the concentration of H<sub>2</sub> declined slowly from 25,000 ppm to 21,000 ppm within 20 h (declined by 17 %). In a similar time window (21 h). 2 Pt/CN180 and 2.5 Pt/CN180 reduced the H<sub>2</sub> concentration by 38 % and 83 %, respectively, while all the H<sub>2</sub> is eliminated within 5 h when using 3 Pt/CN180 or 1.5 Pt/CN0. These results suggest that the metallic Pt NPs are very active towards the backward reaction so that H<sub>2</sub> and O<sub>2</sub> can hardly coexist. Such backward reaction was also observed in our CN30 and CN90 samples (shown in Figure S3b) as well as the reported  $Pt/g-C_3N_4$  nanosheets [25]. We believe that the relative activity between the forward and backward reactions determines the overall reaction. Previous research in electrocatalysis showed that Pt single atoms in their oxidation state were almost inert to ORR process [53], consistent with our finding. So far, the backward reaction is still one of the main hurdles of overall water splitting and the most popular strategy is to coat an oxide layer (e.g. MoO<sub>x</sub>, CrO<sub>x</sub>) on the metal NPs (e.g. Pt, Rh) [56,57]. The layer protects the metal catalysts from contacting the locally generated O2 while minimally impacting the hydrogen production reaction. Our findings show that downsizing the Pt cocatalyst can selectively suppress the unwanted backward process while maintain the forward H<sub>2</sub> evolution.

To further understand the origin of the activity of laser exfoliated g- $C_3N_4$ , we investigated its band edge positions. UV–vis diffuse reflectance spectrum (UV–vis DRS) and the related Kubelka-Munk plots demonstrated that the bandgaps of CN0 and CN180 powders were 2.81 and 2.96 eV, respectively. (Fig. 6a and b). The blue shift of the absorption (Fig. 6a) and the increased bandgap of CN180 were due to the quantum confinement effect [58]. Moreover, the XPS results show that



**Fig. 4.** (a) and (b) TEM images of Pt/CN0. (c) HRTEM images of Pt/CN0. (d) TEM image of Pt/CN180. (e) HRTEM image of Pt/CN180. (f) HAADF-STEM image of Pt/CN180. (g-j) EDS mapping of Pt/CN180. (k) XPS-Pt 4f spectra of CN0 and CN180 with  $\sim 1.4$  wt.% of Pt. (l) the structure model of Pt/g-C<sub>3</sub>N<sub>4</sub> with a Pt atom in a six-folder cavity. (m) the structure model of Pt/g-C<sub>3</sub>N<sub>4</sub> with a Pt atom on a -C=N defect site.



**Fig. 5.** (a) the effect of Pt loading on  $H_2$  production in the presence and absence of methanol (MeOH). The red solid bars (left) show the hydrogen production in pure water for 6 h. The black bars (right) show the hydrogen production in 20 vol.% aqueous solution of methanol for 1 h. (b) the effect of Pt loading on CN180 on the  $H_2$  oxidation reaction (*i.e.* the backward reaction) (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

the valence band maximum of g-C<sub>3</sub>N<sub>4</sub> downshifted continuously from 2.17 eV to 2.48 eV (vs. the fermi level) with the laser exfoliation (Fig. 6c). The absolute band edge positions were obtained by measuring the work functions (i.e. Fermi levels) of CN0 and CN180 with a Kelvin probe (work functions shown in Figure S8). As summarized in Fig. 6d, CN0 has a conduction band edge at - 0.71 eV and a valence band edge at 2.1 eV, while CN180 has a conduction band edge at - 0.46 eV and a valence band edge at 2.50 eV. Therefore, the total shift of the valence band edge was 0.4 eV. In fact, band edge shifting has been frequently reported in g-C<sub>3</sub>N<sub>4</sub> materials [34,37,39,43]. Usually, a decrease of either the thickness or the crystallinity induce upward shift of the conduction band and valence band edge positions [34,43], which is opposite to what we observed here. On the contrary, downward shifts of band edge positions have been observed in thermally-treated g-C<sub>3</sub>N<sub>4</sub> in the presence of NaBH4 or in a N2 atmosphere, both of which created -C = N defects [37,39]. Their DFT calculations confirmed that the introduction of the electrophilic  $-C \equiv N$  defects lowered the band edge positions [37]. Therefore, it was the decoration of -C = N defects, rather than the exfoliation, dominated the shifting direction. The downward shift of the valence band edge position, in principle, made the holes

more powerful in water oxidation reaction.

The effect of laser exfoliation on charge separation have be studied by photoluminescence (PL) and electrochemical analyses. Fig. 7a showed a strong PL peak at 459 nm for CN0 and it was remarkably reduced and blue-shifted after the laser treatment. The blue shift agrees with the UV-vis results in Fig. 6a due to decreased size and thickness, while the reduced intensity of PL suggested an efficient separation of photo-excited electrons and holes [37,43]. Time-resolved PL (Fig. 7b) showed that the lifetimes of the charge carriers increased from 12.6 ns to 21.2 ns after 3 h of laser processing, in consistence with conventionally exfoliated g-C<sub>3</sub>N<sub>4</sub> nanosheets [36,59]. The photo-excited electrons and holes in CN180 thus have more time to participate in the surface reactions. Electrochemical analysis showed that CN180 has a larger photocurrent (Fig. 7c) and a smaller hemicycle radius in the electrochemical impedance spectroscopy (Fig. 7d), indicating more efficient production of photo-excited electrons and holes as well as faster transfer kinetics. Combining the PL and electrochemical results, we confirmed that the laser exfoliation facilitated the production, separation, and transfer of the photoelectrons and holes in g-C<sub>3</sub>N<sub>4</sub>. This property was mainly ascribed to the reduced thickness and lateral size,



Fig. 6. (a) the UV–vis diffuse reflectance spectra of CN0 and CN180. (b) the bandgaps of CN0 and CN180 calculated through Tauc plot. (c) XPS-VB spectra of CN0, CN90 and CN180; (d) the band edge positions of CN0 and CN180.



Fig. 7. Photoluminescence and electrochemical analyses. (a) photoluminescence of CN0, CN90, and CN180. Excited by 351 nm laser. (b) time-resolved PL spectra of CN0 and CN180. (c) transient photocurrent of CN0 and CN180. (d) electrochemical impedance spectra of CN0 and CN180.

which shortened the charge transfer paths [36,42]. Besides, the electrophilic -C=N groups on the surface might also trap photoelectrons and facilitated the charge separation [37].

#### 3. Conclusions

In conclusion, two-dimensional g-C3N4 nanosheets were successfully activated in the photocatalytic overall water splitting by using a pulsed laser exfoliation method. Compared to the conventional exfoliation that mainly break the weak van der Waals bonds between the  $C_3N_4$  layers, the femtosecond laser pulses break the stronger C–N covalent bonds and cleave the s-triazine units as well, creating abundant  $-C \equiv N$  defects on the new surface. These  $-C \equiv N$  defects not only help g-C<sub>3</sub>N<sub>4</sub> anchor Pt atoms but also shift down its band edge positions. The atomically dispersed Pt provide more active sites for the surface reaction; meanwhile, they suppress the back-oxidation of H<sub>2</sub>, thus allowing the coexistence of H<sub>2</sub> and O<sub>2</sub> products. Besides atomic cocatalyst, the lowered valence band edge position of g-C<sub>3</sub>N<sub>4</sub> has also enhanced the oxidation power of the holes and facilitate the water oxidation reaction. This work clarified the importance of Pt cocatalyst in Pt/g-C<sub>3</sub>N<sub>4</sub> systems towards the photocatalytic overall water splitting, and it provided a new strategy to engineer and activate layered photocatalysts.

#### Credit author statement

Chunzheng Wu and Shengyang Xue prepared and characterized the samples, did the photocatalytic tests, and drafted the manuscript. Zhaojun Qin tested photoluminescence.

Masoumeh Nazari and Hadi Ghasemi measured AFM.

Guang Yang, Shuai Yue and Tian Tong built the laser system. Francisco C. Robles Hernandez measured TEM/HRTEM/EDS/ HAADF-STEM.

Sichuang Xue, Di Zhang and Haiyan Wang measured HAADF-

#### STEM.

Zhiming M. Wang, Shengyan Pu, and Jiming Bao finalized the manuscript.

### **Declaration of Competing Interest**

The authors declare that there is no conflict of interest.

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#### Appendix A. Supplementary data

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