

Frictional Reduction with Partially Exfoliated Multi-Walled Carbon Nanotubes as Water-Based Lubricant Additives

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In this work, partially exfoliated multi-walled carbon nanotubes (Px-CNTs) were prepared by oxidizing multi-walled carbon nanotubes (MWCNTs) and applied into water-based lubricant as a kind of new additives, resulting in an outstanding anti-friction effect. The Px-CNTs have the structures of both MWCNTs and graphene oxide nanoribbons (GONRs). The special structure could prevent aggregation in water-based lubricant and reduce friction effectively. At the same time, Px-CNTs generate both sliding and rolling friction like MWCNTs and GONRs simultaneously. The friction force of Px-CNTs tended to go up after declining with increasing its loading, suggesting the existence of optimum additive amount of additions. Compared with water, water with 0.5 wt% Px-CNTs further reduced the friction force up to 66.4%. Compared with CNTs-COOH and GONRs dispersed in water via a similar method, Px-CNTs in water displays remarkable friction characteristic, suggesting that the friction force of water with 0.5 wt% Px-CNTs is decreased by 19.82% and 13.82% compared with water with 0.3 wt% MWCNTs and GONRs.

Keywords: Water-Based Lubricants, Carbon Nanomaterials, Partially Exfoliated, Anti-Friction.

1. INTRODUCTION

The dramatic increase of industry activities like transportation, machinery and chemical engineering causes percussive consumption of non-renewable energy. Friction and wear aggravate the non-necessary energy costs, and lubricants are applied to reduce this dissipation. Compared with traditional lubricating oil, water-based lubricants have better prospective applications due to the inexpensive and environmental-friendly properties.^{1,2} Nano materials, especially carbon nanomaterials have attracted broad attentions.^{3–5} Carbon nanomaterials have development trend in abundant fields, such as machinery, electricity and sensors.^{6–8} Since fullerene was utilized as antifriction wear since the 1990s,⁹ good tribological performance of carbon nanomaterials caused enormous development as potential lubricating additives.^{10,11} Multi-walled carbon nanotubes

(MWCNTs) and graphene are two typical water-based nano-antifriction additives.

Lubricants generally worked by forming thin layers of flat physical tribofilm on frictional surfaces, however, normally with certain proportions of surface exposure. For example, MWCNTs accommodate in these grooves of surface, preventing direct contact, and reduce friction and wear. Meanwhile, owing to the roll-like shape, MWCNTs have the potential to reduce resistances by changing sliding frictions into rolling frictions.^{12,13} Functional dispersion suggests MWCNTs with excellent tribological characteristic, high load-carrying capacity, and good anti-wear property with limited friction in ultimate pressure.¹⁴

Graphene, with the naturally two-dimensional character, slides easily between layers, indicating its potential as antifriction materials.^{15,16} The extremely good properties of graphene materials, like the controllability of thermal conductivity, high chemical inertness, and good

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fabricability, allow its broad utilization in nanoscale.¹⁷ However, the innately hydrophobicity of graphene limits its application as water-based lubricant additives. Graphene oxide (GO), considered as a graphene derivative, was first developed as a graphene precursor, while the functional oxygen atoms are found to force its dissolution in water, proposing the non-necessity of hydrophilic treatment. Both MWCNTs and graphene derivatives suggest good properties in friction and wear reduction, however, the large length-diameter ratio and the slenderness structure lead to incidental entanglement of MWCNTs; while in the graphene systems, the extended π -conjugation may cause strong π - π interaction and Van der Waals force, resulting in strong tendency of graphene sheets to form irreversible agglomeration.

To overcome the threshold of MWCNTs and graphene, a novel carbon nanomaterial: partially exfoliated multi-walled carbon nanotubes (Px-CNTs), is developed. Px-CNTs is a type of carbon nanotubes partially coated by nanoribbons which are like graphene oxide sheets in the long shape. Being considered as a combination of MWCNTs and graphene, Px-CNTs generate enhanced capacitance than MWCNTs due to the improvement of effective surface area and defect density of the exfoliated tubular structures.^{18,19} Different from pure MWCNTs, the long-shaped nanotubes structure of Px-CNTs prevents the nanoribbons from agglomeration. Meanwhile, the internal walls of Px-CNTs still keep intact like MWCNTs, with the external tubes exfoliated into nanoribbons to reduce entanglement.

In this work, the Px-CNTs were prepared by oxidizing MWCNTs and the characterization of Px-CNTs was presented. The Px-CNTs were applied as water-based lubricant additives. Both the contribution of the special structure of Px-CNTs in preventing aggregation in water-based lubricant and reducing friction effectively and the tribological properties of Px-CNTs were discussed with a comparison with pure water, and aqueous solutions containing CNTs-COOH and GONRs.

2. EXPERIMENTAL DETAILS

2.1. Materials

MWCNTs (95%) were purchased from Nanjing XFNANO material Tech. Co. Ltd. Hydrogen peroxide (H_2O_2), phosphoric acid (H_3PO_4), nitric acid (HNO_3), sulphuric acid (H_2SO_4), hydrochloric acid (HCl) and potassium permanganate (KMnO_4) were purchased from Sinopharm Chemical Reagent Company.

2.2. Preparation of the Materials

2.2.1. Preparation of CNTs-COOH

CNTs-COOH were prepared by acidification of MWCNTs with acid. 1 g MWCNTs powders were dispersed to the mixture of 100 mL H_2SO_4 and 33 mL HNO_3 . The mixture was stirred at 60 °C for 3 h. The reaction was terminated

by adding 1000 mL distilled water and 10 mL 30% H_2O_2 solution. The solid product was washed by 5% HCl and followed by distilled water washing it to neutral. Then the solid was dried in a vacuum oven at 70 °C for 24 h to obtain CNTs-COOH.

2.2.2. Preparation of Px-CNTs

Px-CNTs were prepared through following method. 1 g MWCNTs powders were dispersed into 60 mL H_2SO_4 and stirred for 1 hour. Then 12 g KMnO_4 was gradually added into the mixture. The solution was stirred at 50 °C for 0.5 h to obtain partially exfoliated multi-walled carbon nanotubes. The reaction was terminated by adding 1000 mL distilled water and 12 mL 30% H_2O_2 . After washing by distilled water, the Px-CNTs were dried in a vacuum oven at 75 °C for 36 h.

2.2.3. Preparation of GONRs

GONRs were prepared by oxidizing MWCNTs. 1 g MWCNTs was dispersed into 60 mL H_2SO_4 and stirred for 1 hour. Then 12 g KMnO_4 was gradually added into the mixture. The solution was stirred at 50 °C for 3 h to obtain GONRs. The reaction was terminated by adding 1000 mL distilled water and 12 mL of 30% H_2O_2 . After washing by distilled water, the solid was dried in a vacuum oven at 75 °C for 36 h.

2.3. Characterizations

The microstructures of the target products were investigated by transmission electron microscopy (TEM, JEOL JEM-2100). X-ray diffraction (XRD) measurements were collected using an X-ray diffractometer (D8 Advance, Bruker) with Cu K α radiation ($\lambda = 1.5418$ nm) at a scanning rate of 10° min⁻¹ in the 2 θ range from 5° to 90°. Raman spectroscopy (Horiba Jobin Yvon HR800, France) and Fourier transform infrared spectroscopy (Thermo Nicolet5700, USA) were used to analyze the chemical structure of products.

2.4. Tests for Tribological Properties

The as-prepared CNTs-COOH, Px-CNTs and GONRs were dispersed into distilled water by ultra-sonication to prepare dispersion with different concentration. The tribological properties tests of water with Px-CNTs were taken on a UMT-2 ball-plate machine, compared with pure distilled water, water with CNTs-COOH and water with GONRs. With a rotating speed of 120 rpm, the diameter of 1 cm and a load of 5 N were taken for a 10-min continuous test. The diameter of the balls used in the tests was 1.58 mm. The balls were made of GCr15 bearing steel. Both balls and stainless steel disk used in the tests were cleaned with 10 min ultra-sonication in absolute ethyl alcohol after 10 min ultra-sonication, and then were dried after flushing. The wear scar was measured by optical

microscope (Tuanjie, XRP-700V, China) on the stainless steel disk after friction.

3. RESULTS AND DISCUSSION

The prepared carboxylic multi-walled carbon nanotubes (CNTs-COOH), Px-CNTs, and graphene oxide nanoribbons (GONRs) were reported as three potential nano-antifrication materials. MWCNTs were first dispersed into sulfuric acid and stirred into a homogeneous mixture, followed by the addition of oxidation agent. CNTs-COOH were prepared as a non-exfoliated comparison, with the carboxyl group increasing the hydrophilicity. To increase the oxidation efficient, nitric acid was added together with sulfuric acid as oxidation source to generate CNTs-COOH. Meanwhile, Px-CNTs and GONRs were exfoliated by utilizing potassium permanganate, and the further stirred at 50 °C to control the exfoliation degree of CNTs.^{20,21} The reaction was quenched by the addition of hydrogen peroxide aqueous solution.

Compared with MWCNTs (Fig. 1(a)), CNTs-COOH have a similar tubular structure with a diameter around 45 nm, while with rough surface, sharp outline and defects at the end of tubes (Fig. 1(b)). Due to the heavy strain of the hexagon-heptagon pairs, the functionalization with

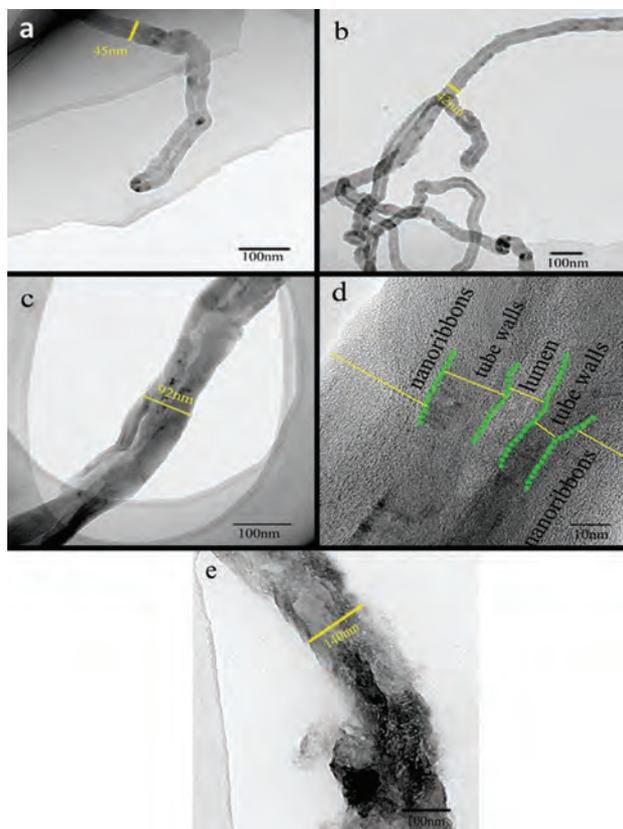


Figure 1. TEM microstructures of (a) MWCNTs, (b) CNTs-COOH, (c) Px-CNTs, (d) a magnifying part of (c) showing the structure of Px-CNTs in detail with the combination of nanotubes and nanoribbons, and (e) GONRs.

carboxylic acid (COOH) groups usually occurs at the end and sidewalls of the nanotubes.²²⁻²⁵ During the permanganate oxidation, the unzipping process from tubes into ribbons was largely extended along the width of surface, leading to a blurry surface of GONRs (Fig. 1(e)). The thorough exfoliation generates GONRs with a non-tubular structure, and the diameter is beyond 140 nm. The TEM picture of Px-CNTs suggests a structure between nanotubes and nanoribbons (Fig. 1(c)), with the nanotubes covered with partially unzipped ribbons, and blurry edge. The diameter of Px-CNTs (around 90 nm) is assumed to be a result of combined interaction of unfolded walls and the intact lumens, which localized between the range of MWCNTs and GONRs. Figure 1(d) presents a clear existence of both exfoliated ribbons and the intact tubular portion in one Px-CNT particle.

The FTIR spectra were utilized to detect the oxidation degree of MWCNTs, CNTs-COOH, Px-CNTs and GONRs (Fig. 2). The peaks located at 3400 and 1590 cm^{-1} are assigned to the stretching vibration and bending vibration of water molecules. The peaks of 3145 and 1384 cm^{-1} are ascribed to the stretching and flexural vibration of the structural hydroxyl groups. The stretching vibration of carboxyl and carbonyl at the edge presents at 1714 cm^{-1} . The epoxy group and phenolic hydroxyl group are proved by the peaks of 1220 and 1033 cm^{-1} . Px-CNTs and GONRs present similar trace with same bands, and the higher peak intensity of GONRs suggests a higher degree of oxidation.

From the XRD patterns of MWCNTs, CNTs-COOH, Px-CNTs and GONR (Fig. 3), almost identical diffractograms are observed for CNTs-COOH. There is an intense and sharp diffraction peak at $2\theta = 26.13^\circ$ on the diffractograms of both samples, indicating an interplanar spacing of 0.34 nm. However, the diffraction peak at $2\theta = 26.13^\circ$ of Px-CNTs reveals the tendency of weakness. At the same time, a new peak at 11.36° emerges, stemming

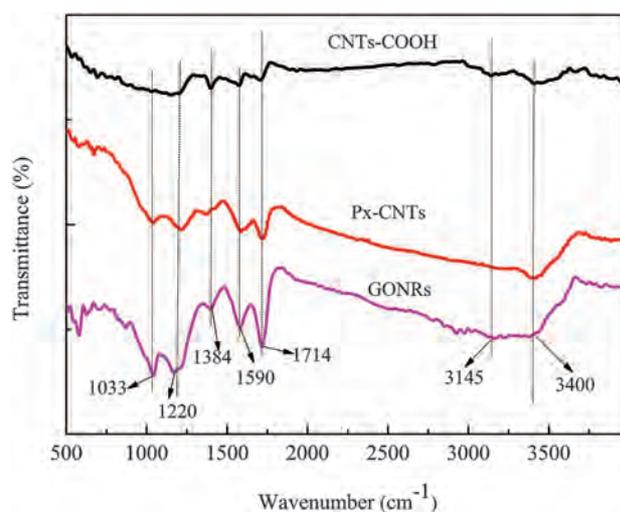


Figure 2. FTIR absorption spectra of MWCNTs, CNTs-COOH, Px-CNTs and GONRs.

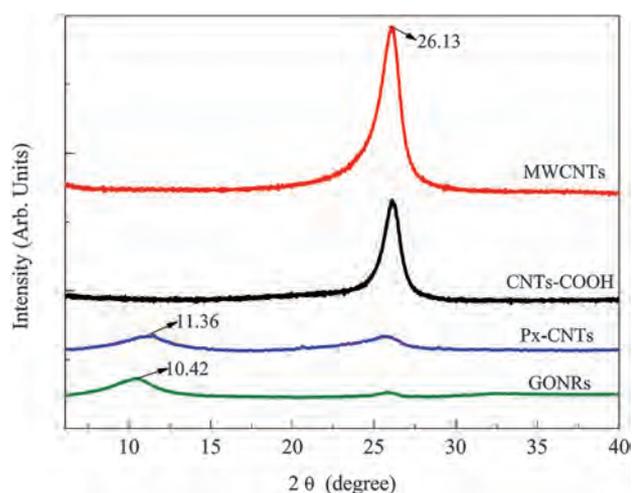


Figure 3. Typical XRD patterns of MWCNTs, CNTs-COOH, Px-CNTs and GONR.

from the increasing layer spacing during introducing the oxygen-containing functional groups that lead to the wrinkles of structure of carbon atom layer and the insertion of hydrone between layers. With further oxidation, GONR shows an almost invisible peak at 26.13° , revealing that the sample was oxidized almost completely. At the same time, the graphene oxide characteristic peak shifts left to 10.42° . The interlayer spacing runs up to 0.85 nm.

The structure of target samples was further researched by Raman spectroscopy (in Fig. 4). As displayed, MWCNTs, CNTs-COOH, Px-CNTs and GONRs have similar Raman spectra. They all present D band and G band at 1359 cm^{-1} and 1576 cm^{-1} , respectively. The G band is generated by stretching vibration of C–C, while the D band is caused by sp^3 carbon atom. In the investigation of carbon materials, the relative intensity ratio of G band and D band (I_G/I_D) is commonly used to characterize the order of the structure. From above to below in Figure 4,

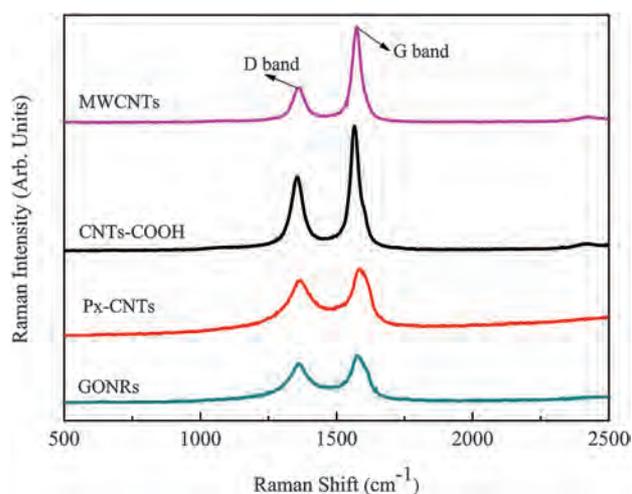


Figure 4. Raman spectroscopy of MWCNTs, CNTs-COOH, Px-CNTs and GONRs.

with the I_G/I_D of the four samples progressive decreased, the degree of order from MWCNTs to GONRs declines. The number of oxygen-containing functional groups was increased as the oxidation and exfoliation degree was enhanced, resulting in an incremental disorder and higher amount of defects in the surface and edge.

To figure out the antifriction effect of Px-CNTs, five aqueous solutions with different concentrations of Px-CNTs were prepared respectively. The mechanism of water-based lubricant with Px-CNTs in Figure 5 presents the synergistic effect of the parts of nanotubes and nanoribbons, showing homogeneous dispersion of Px-CNTs between friction surfaces. The Px-CNTs have both structure of nanotubes and nanosheets, which generates both sliding and rolling friction like MWCNTs and GONRs simultaneously. The Px-CNTs deposit in the grooves of the surface and adsorb on the friction surface, while the layer nanosheets provide easy sliding and the tube behaves as rolling bearings. At the same time, the special structure of Px-CNTs could reduce agglomeration. On one hand, the nanosheets structure can prevent nanotubes from entanglement. On the other hand, the structure of nanotubes can stop the nanosheets from agglomeration.

Px-CNTs were dissolved in purified water at a series of concentration. Figure 6 shows the variations of friction force suggested by the UMT-2 ball-plate machine with a rotating speed of 120 rpm, diameter of 1 cm and a load of 5 N, with the test continuously lasting for 10 minutes. Generally, the friction of the six samples went down gradually. At first, the solution filled into the gaps between friction surfaces. And then, the Px-CNTs were absorbed on the friction surfaces to form a thin, even physical tribofilm on the friction surfaces, preventing direct contact of friction surface. Due to the tribofilm, the friction force goes down and becomes stable. Water was used as comparison, showing an anti-friction effect, and all the aqueous solutions with different Px-CNTs contents provide remarkable lower friction. Especially, the addition of Px-CNTs further reduced the friction force up to 66.4% (0.5 wt% of Px-CNTs), compared with water.

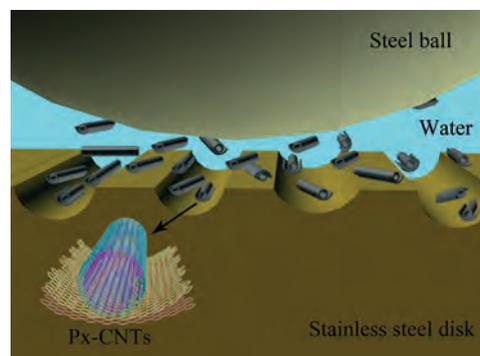


Figure 5. The mechanism of water-based lubricant with Px-CNTs presents the cooperation effect of the parts of nanotubes and nanoribbons. Inset: the schematic diagrams of Px-CNTs.

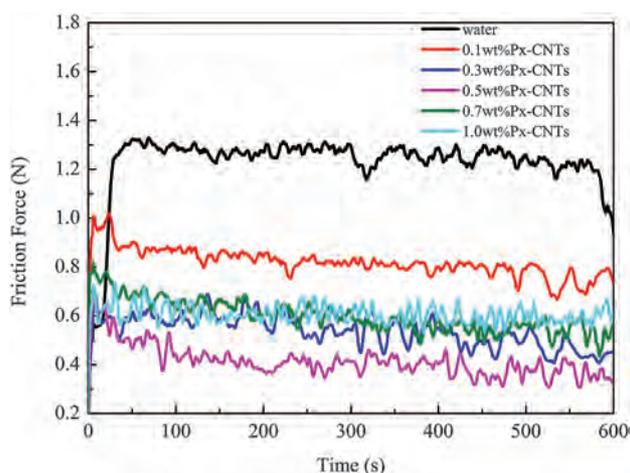


Figure 6. The variations of friction force of a series concentration of Px-CNTs compared with water, displaying remarkable anti-friction property.

Similar investigations of CNTs-COOH and GONRs were carried out under the same condition, Figure 7. All three nano-materials reduced the friction force compared with water, while Px-CNTs suggested to be the best anti-friction additive. The friction force traces were first depressed as the concentration of efficient additives increased, and the snarling effect gradually reduced the valid nano-particles, resulting in the inefficient additives. The friction force declined first and then increased gradually with increasing the content, indicating the presence of an optimum concentration of additives. After the comparison of the three lines of friction force, we could conclude that the friction force of CNTs-COOH and GONRs is lower when the content of samples is below 0.5 wt%. The reason is that the concentration is so low that the nanotubes and nanoribbons could be dispersed in water. However, when the concentration reaches 0.5 wt%, the agglomeration of CNTs-COOH and GONRs gets worse. And the combination structure of Px-CNTs is claimed to

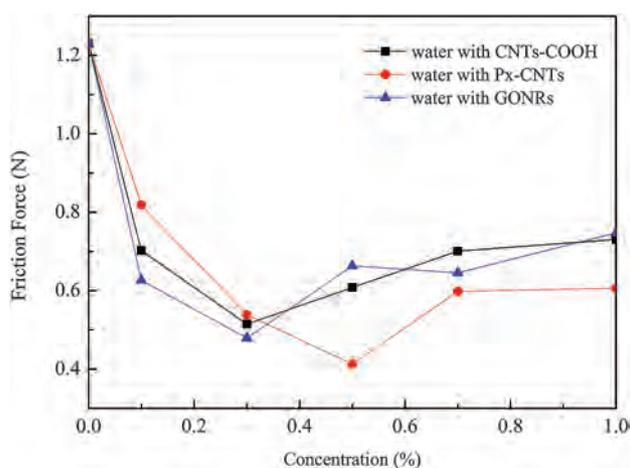


Figure 7. Friction force as a function of CNTs-COOH, Px-CNTs or GONRs concentration.

decay the snarling as both the entanglement and agglomeration, so the friction force of Px-CNTs is the lowest among these three carbon nanomaterials after the concentration arriving at 0.5 wt%. Besides, the structure of Px-CNTs could reduce agglomeration, therefore, postponing the most effective concentration point to 0.5 wt% compared with 0.3 wt% of CNTs-COOH and GONRs. At the same time, the friction force of water with 0.5 wt% Px-CNTs is decreased by 19.82% and 13.82% compared with water with 0.3 wt% MWCNTs and GONRs.

4. CONCLUSION

In summary, Px-CNTs, prepared through unzipping MWCNT by oxidation, could be dispersed homogeneously in water on account of the introduction of carboxyl, hydroxyl and epoxy groups onto the edge and surface of Px-CNTs. The aqueous solutions with CNTs-COOH, Px-CNTs properties compared with water. Particularly, water with Px-CNTs at 0.5 wt% content displayed an outstanding friction characteristic compared with Px-CNTs at 0.5 wt% content displayed an outstanding friction characteristic compared with CNTs-COOH and GONRs. The structure and friction test of Px-CNTs indicated that the Px-CNTs dispersion entered between the contact surfaces to form a physical tribofilm to prevent direct contact. At the same time, the Px-CNTs deposited in the grooves of the surfaces and adsorbed on the friction surfaces, while the layer nanosheets provided easy sliding and the tubes behaved as rolling bearings. Moreover, Px-CNTs had both structure of nanosheets and nanotubes. The parts of nanotubes and nanoribbons, which prevent entanglement and agglomeration with each other, generated effect of antifricition simultaneously. The Px-CNTs suggest good properties in friction reduction as water-based lubricant additives.

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