Analysis of the mechanism of formation and growth of carbon nanostructures produced through the mechanical milling of graphite

Análisis del mecanismo de formación y crecimiento de nanoestructuras de carbono obtenidas por molienda mecánica de grafito

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Key Handbooks

The research presented here contributes significantly to the field of nanotechnology by offering a simple and versatile method for the production of carbon nanostructures. This chapter compares two mechanisms for the formation of carbon nanostructures, both using mechanical milling (MM) and heat treatment (HT). X-ray diffraction (XRD), Raman spectroscopy and high-resolution transmission electron microscopy (HRTEM) characterisation techniques were employed. By varying the milling times of crystalline graphite with AlCuFe quasicrystals and amorphous graphite, nanostructures are defined as the milling time increases. The quasicrystal acts as an accelerating agent in the reduction of the crystal size during the process and often assists in the generation of carbon nanostructures. Heat treatment between 200 °C and 450 °C best defines onion-type nanostructures (nano-onions) and curved rolls.

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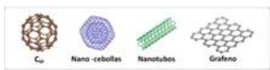
Abstract

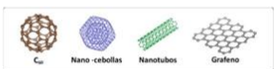
A microstructural analysis was conducted to investigate the formation mechanism of carbon nanostructures produced through mechanical milling crystalline and amorphous graphite, followed by thermal treatments at various temperatures. A unidirectional ball mill operating at 1700 rpm was employed for the synthesis. Different milling times (3, 6, and 12 hours) and heat treatments were used at 200 °C, 300 °C, and 450 °C. Results obtained by X-ray diffraction, Raman spectroscopy, and high-resolution transmission electron microscopy revealed the formation of curved concentric nuclei composed of carbon layers for milling times of 6 and 12 hours. The thermal treatment at 450°C promoted the growth and definition of carbon nano-onions.

Analysis of the mechanism of formation and growth of carbon nanostructures produced through the mechanical milling of graphite		
Objectives	**Methodology**	**Contribution**
 Study the growth of carbon nanostructures through thermal processing.	 Crystalline graphite with quasicrystals and amorphous graphite are subjected to different milling times and temperatures.  XRD, Raman, and HRTEM characterization.	$Al_{64}Cu_{24}Fe_{12}$ The quasicrystal acts as an accelerator in the creation of nanostructures.  Applying TT between 200°C and 450°C helps to better define the nanostructures.

Microstructural, nanostructures, synthesis

Resumen

Se realizó el análisis microestructural del mecanismo de formación de nanoestructuras de carbono obtenidas por molienda mecánica de grafito cristalino y amorfo, las cuales fueron crecidas por tratamiento térmico a diferentes temperaturas. Para la síntesis de nanoestructuras de carbono se empleó un molino mecánico unidireccional que oscila a 1700 rpm. Las variables de experimentación fueron los diferentes tiempos de molienda (3, 6 y 12 h) y los tratamientos térmicos a 200 °C, 300 °C y 450 °C. Las técnicas de caracterización de difracción de rayos X, espectroscopía Raman y la microscopía electrónica de transmisión de alta resolución indican la formación de núcleos concéntricos curveados de láminas de carbono para tiempos de molienda de 6 y 12 h. Con el tratamiento térmico a 450 o C se apreció un crecimiento y definición de nano-onions de carbono (nanocebollas).

Análisis del mecanismo de formación y crecimiento de nanoestructuras de carbono obtenidas por molienda mecánica de grafito		
Objetivos	**Metodología**	**Contribución**
 Determinar el crecimiento de nanoestructuras de carbono al aplicar tratamiento térmico.	 Se someten grafito cristalino con cuasicristales y grafito amorfo a distintos tiempos de molienda y temperaturas.  Caracterización con DRX, Raman y HRTEM.	$Al_{64}Cu_{24}Fe_{12}$ El cuasicristal actúa como un acelerador en la creación de las nanoestructuras  Aplicar TT a 200 °C a 450 °C logra definir mejor las nanoestructuras

Microestructural, nanoestructuras, síntesis

Introduction

Since the discoveries of fullerenes, carbon nanotubes, graphene and other allotropic forms of carbon, the search for an increasingly simple and economically viable process has been a challenge for science today. The synthesis of carbon nanostructures by mechanical methods has been novel in recent years because of its versatility and ease of designing mechanical mills at different speeds. High-energy ball milling (spex milling) of graphite in an air atmosphere leads to forming time-dependent carbon nanostructures through mechanical deformation (Patiño et al. 2020). Mechanical crushing facilitates the synthesis of carbon nanostructures and inducing high temperatures with controlled atmospheres enables gas-phase reactions that produce unique shapes such as carbon nanotubes and carbon nanobeads. (Satoshi et al. 2011).

Heat treatment significantly influences the properties and performance of carbon nanostructures, improving their properties. Several studies show that heat treatment can improve the structural uniformity and overall performance of carbon nanomaterials (Carneiro and Simões, 2021; Villacorta et al. 2013; Srikanth et al. 2016).

Therefore, in this research the formation of carbon nanostructures from the mechanical milling of crystalline and amorphous graphite is exposed, employing a unidirectional mill where, subsequently, from this process, a heat treatment is applied.

Methodology

Hexagonal and amorphous graphite powders were subjected to mechanical deformation by high energy mechanical milling. The mill comprises a one-way oscillating mechanical system connected to a Siemens electric motor (1750 rpm at a speed of 5 m/s). The operation varies according to the time and ratio between the balls and the sample's weights, as shown in table 1.

Box 1

Table 1

Ratio of media weight to sample weight, varying the grinding time

	Graph		
	Crystalline	Amorphous	
Ratio	20:1	8:1	16:1
Milling hours	3	3	3
	6	6	6
	12	12	

Source: *Own elaboration*

Martínez González (2018) employed a hexagonal graphite together with quasicrystalline icosahedral Al-Cu-Fe particles for their synthesis by milling at a weight ratio of 20:1 for the milling times of 3, 6 and 12 hours. While Valladares Gómez (2018), an amorphous graphite with ratios of 8:1 for 3, 6 and 12 hours of milling; and another ratio of 16:1, for 3 and 6 hours of milling. The heat treatment included placing the previously ground powders in hardened steel crucibles. They were then placed in a muffle-type electric furnace in an air atmosphere at temperatures, as shown in table 2, with an exposure time of 5-6 hours, after which they were allowed to cool to room temperature.

Box 2

Table 2

Heat treatment temperatures of the samples in an air atmosphere

Graph	Temperatures (° C)		
Crystalline (6 h of HT)	200	350	450
Amorphous (5 h of TT)	250	300	450

Source: *Own elaboration*

To determine the main characteristics of the formation and growth of carbon nanostructures in each process, the samples were characterised using X-ray diffraction (XRD), Raman spectroscopy, and transmission electron microscopy (TEM).

Results

Figure 1a shows the X-ray diffraction patterns of the samples subjected to 0, 3 and 6 h of mechanical milling of crystalline graphite (C) with the quasicrystalline phase i-Al-Cu-Fe (both i+C phases) at a 20:1 ball to sample weight ratio. Pattern 1a) shows the mixing of the powders (0 hours) where the typical quasicrystalline i-phase with the hexagonal graphite (C) phase can be seen. A very intense peak located around $2\theta \approx 26.55°$ is observed, which corresponds to the crystallographic plane (002) of the hexagonal graphite, a weaker peak is also observed at $2\theta \approx 54.68°$ corresponding to the plane (004). In the diffractograms corresponding to (b) and (c) with milling times 3 and 6 hours, respectively, a decrease in intensity and broadening of the main graphite peak (002) can be seen, thus indicating a significant decrease in crystal size. From this result, it can be deduced that the graphite is being crushed to smaller and smaller crystal dimensions as a function of milling time. Figure 1b) shows a 2θ magnification of the main peak (002) to observe a shift to the left as a function of milling time. This result shows a growth in the interplanar distance of the graphite, so it is deduced that the material tends to have a distortion of the structural conforms to it. Thus, these results of decreasing crystal size and distortion of the graphitic planes suggest the formation of new distorted carbon structures. On the other hand, the quasicrystal i remains stable, indicating that it functions as a cutting medium.

Box 3

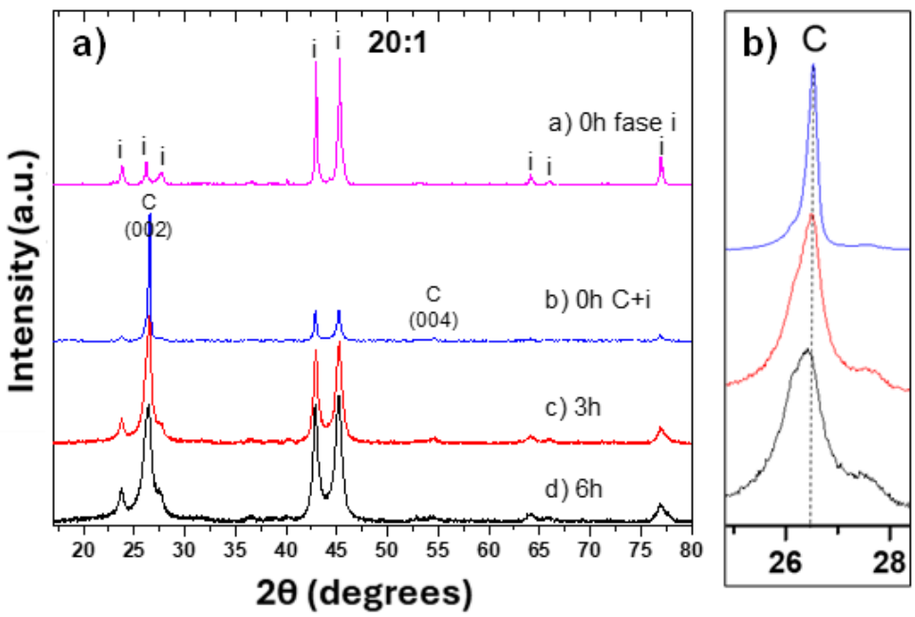


Figure 1

XRD patterns of crystalline graphite C samples with i-phase subjected to different mechanical milling times, a) with a 20:1 ratio, b) enlargement of the 2θ region from 26 to 28 degrees

Source: *Own elaboration*

Figure 2 shows the XRD patterns of amorphous graphite samples subjected to different grinding times with a ball to sample weight ratio of 16:1 and 8:1. For both ball to sample weight ratios, the position of $2\theta \approx 24°$ of the main peak of the hexagonal graphite (002) of the initial amorphous graphite samples can be seen. It is important to mention that graphite has a tiny particle size and a distortion of its structure, as explained above. For the 3 and 6 hours milled samples with a 16:1 ratio, a thinning of the peaks can be observed (002), thus inferring that the mechanical milling promotes the formation or growth of the graphitic planes. However, for the 8:1 ratio, a widening of the peaks occurs, indicating a more significant decrease in crystal size and a shift of the peaks to the right, indicating a slight decrease in the interplanar distance. From these results it can be deduced that mechanical grinding promotes the formation and growth of distorted graphitic planes.

Box 4

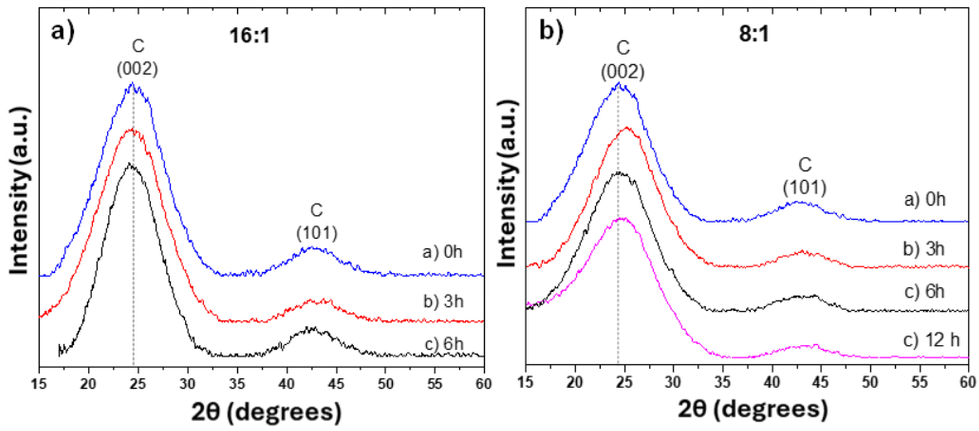


Figure 2

XRD patterns of amorphous graphite samples subjected to different mechanical grinding times with a) 16:1 and b) 8:1 ball to sample weight ratio

Source: *Own elaboration*

The D and G bands are characteristic in graphite and carbon nanostructures for Raman spectroscopy. The D band arises due to defects and disorder in sp2 carbon hybridization and breathing-type vibrational modes of aromatic ring structures. It is located in the range of 1250 cm-1 to 1450 cm-1. G originates from the stretching vibrations of the C-C bonds corresponding to the sp2 hybridization typical of hexagonal graphite, located between 1500 cm-1 and 1600 cm-1. Figure 3 shows the Raman spectra of the samples subjected to mechanical milling, which correspond to a) crystalline graphite milled at a ratio of 20:1, b) amorphous graphite milled at a ratio of 16:1 and c) amorphous graphite milled at a ratio of 8:1. In the spectra a) it can be seen the growth in intensity of the D-band as a function of the milling time, associated with a distortion of the graphitic planes according to the X-ray diffraction results (fig. 1). For the amorphous graphite milling shown in spectra b) and c), a weak growth in intensity of the D-band can be appreciated, however, for the 16:1 milled samples its growth is higher concerning the 8:1. In these results it can be deduced that the quasicrystals together with the balls acted as crushers of the crystalline graphite promoting distortion of the D band, while for the grinding of the amorphous graphite changes are slightly not so noticeable with this technique.

Box 5

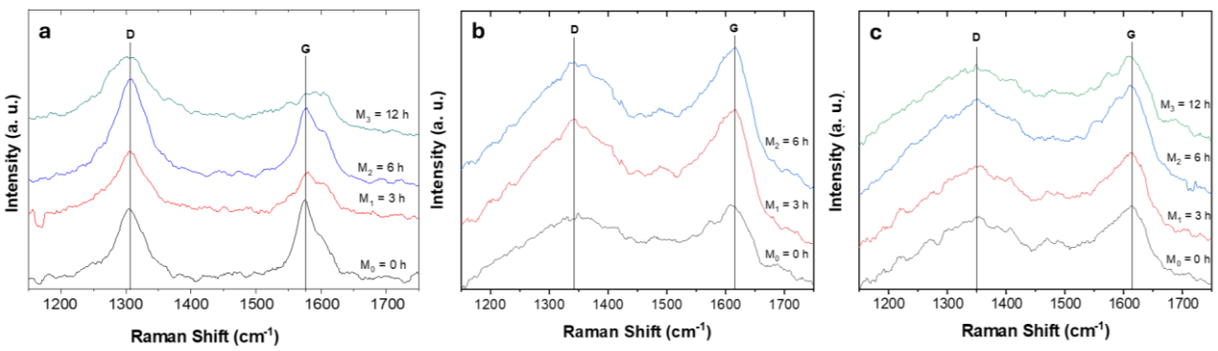


Figure 3

Raman spectra of graphites at different mechanical milling times: a) crystalline + quasicrystalline graphite with a 20:1 ratio, b) amorphous graphite with a 16:1 ratio, and c) amorphous graphite with an 8:1 ratio

Source: *Own elaboration*

Different thermal treatments were carried out to analyse the growth of these nanostructures, using the sample ground for 3 hours of crystalline graphite (20:1 ratio) and amorphous graphite (8:1 ratio). Figure 4 shows the results of each of the spectra and shows an increase in the intensities and a broadening of the D and G bands in the first treated samples. However, when reaching the annealing temperatures of 450 °C, the intensities of the Raman profiles tend to decrease for crystalline graphite since an annealing time of 6 hours has been used while that of amorphous graphite was used for 5 hours.

In both spectra, the growth of the D-band can be significantly noticed, indicating the growth and definition of the carbon nanostructures promoted by the mechanical milling.

Box 6

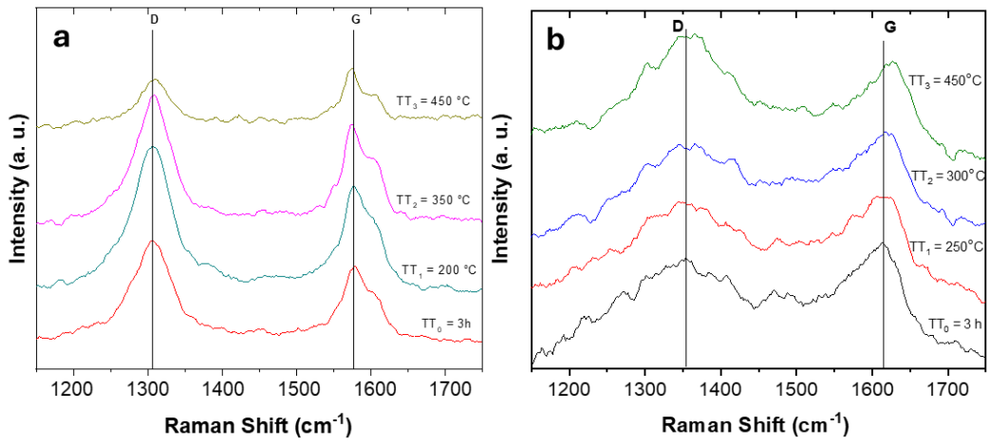


Figure 4

Raman spectra of graphite samples at 3 hours of mechanical milling subjected to different heat treatment temperatures: a) crystalline graphite + i-phase with a 20:1 ratio, b) amorphous graphite with an 8:1 ratio

Source: *Own elaboration*

Table 1 shows the calculated crystal size measurements using the Debye Scherrer formula and the experimental parameters of the XRD profiles. A drastic decrease in the crystal size of the mechanical milling of crystalline graphite can be noticed, thus inferring once again that the milling with the quasicrystalline i-phase has the function of a milling medium. Also, in this table, it is possible to appreciate the effect of the thermal treatment for the milled samples of amorphous and heat treated graphite, where it is possible to find that the thermal treatment temperature of 300 °C has the highest growth percentages and that the samples milled for six h (8:1) and three h (16.1) heat treated at 300 °C achieve 29 and 24 % growth respectively.

Box 7

Table 3

Crystal size according to the Debye-Scherrer formula

Crystalline graphite		Amorphous graphite					
Samples	**Crystal sizes (nm) a MM**	**Samples**	**Crystal sizes (nm) a MM**	**Crystal sizes (nm) a HT 300 ºC**	**% growth**	**Crystal sizes (nm) a HT 400 ºC**	**% growth**
0h	40.84	**0h**	0.892	NA	NA	NA	NA
3h, 20:1	11.84	**3 h, 8:1**	1.039	1.21187	16	1.21648	17
6h, 20:1	11.03	**6 h, 8:1**	0.9806	1.26601	29	1.14433	16
NA	NA	**12 h, 8:1**	1.0531	1.2111	15	1.17832	11
NA	NA	**3 h, 16:1**	0.9838	1.22927	24	1.13429	15
NA	NA	**6 h, 16:1**	1.275	1.20558	3	1.20924	3

Source: *Own elaboration*

High-resolution transmission electron microscopy has been used to analyse the dimensions and shapes of these nanostructures (figure 5). In these images, it is possible to observe the initial formation of curved nanostructures with a certain degree of distortion, shown in figure 5a), which corresponds to the amorphous graphite sample with an 8:1 ratio and 12 hours of milling. Figure 5b) shows the sample heat-treated at 450 °C, where the formation of well-defined nano-blades with sizes around 20 nm can be observed. In the same way, the crystalline graphite samples with the i-phase milled for 3 hours are presented, where distorted and curved graphitic planes are formed. However, with the heat treatment at 200 °C, the growth of elongated nanostructures in the form of rollers is observed.

Box 8

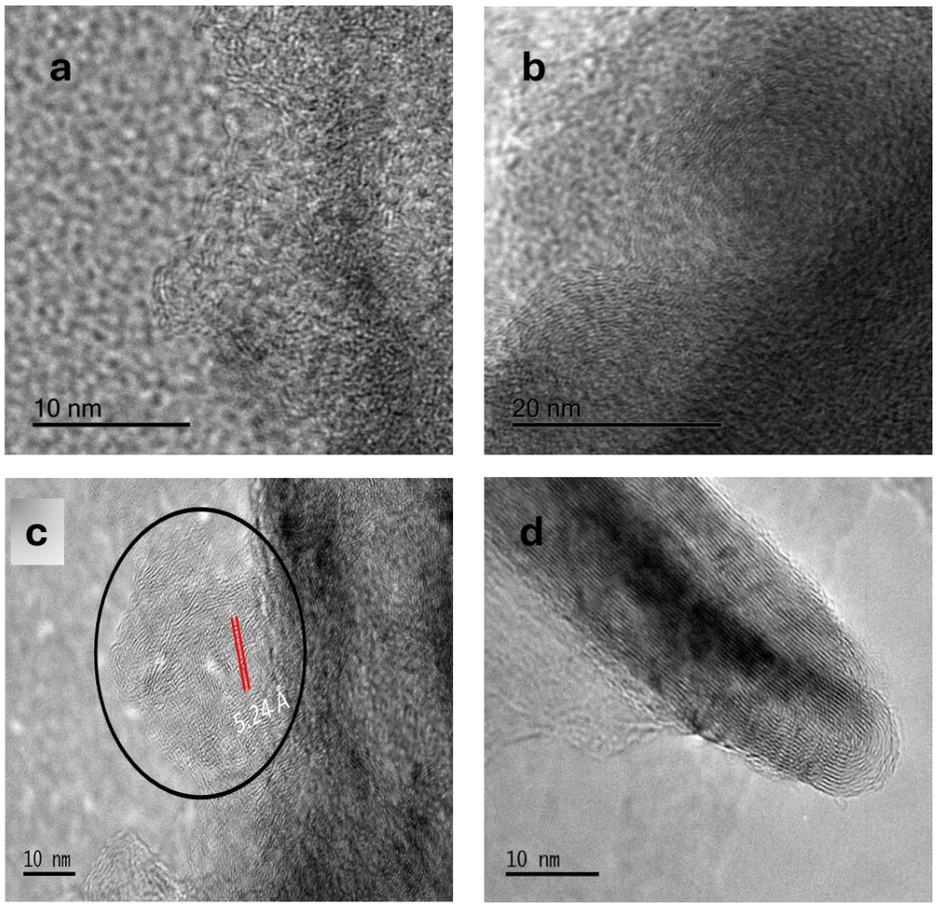


Figure 5

HRTEM of: (a) 12 hours grinding at an 8:1 ratio, (b) 12 hours grinding at an 8:1 ratio and heat treatment at 450 °C, (c) 12 hours grinding at a 20:1 ratio, and (d) 3 hours grinding at a 20:1 ratio and heat treatment at 200 °C

Source: *Own elaboration*

Conclusions

Carbon nanostructures have been formed using a mechanical mill that oscillates in one direction, achieving the formation of carbon nanostructures from crystalline and amorphous graphite.

Mechanical milling under these conditions for crystalline graphite tends to reduce its particle size to nanometric orders, and mechanical milling of amorphous graphite promotes the formation of small curved shapes, giving rise to nanoballs smaller than 10 nm.

The grinding time and the ball weight ratio to sample weight are determining factors in forming carbon nanostructures. This is because, as the duration of the process increases, more nanostructures are generated and tend to adopt a single morphology.

The quasicrystal remained stable and acted as a further milling medium, accelerating crystalline graphite's crystal size reduction process.

The heat treatments could define the nanostructures better, and the optimum temperatures ranged around 300 °C under an air atmosphere.

Declarations

Conflict of interest

The authors declare that they have no conflicts of interest. They have no financial interests or personal relationships that could have influenced this book.

Authors' contribution

Aguilar-Cruz, Felix: contributed to the methodology and writing of the work.
Flores-Gil, Aaron: contributed to the interpretation of the Raman spectra.
Álvarez-García, Emilio: performed the microstructural analysis and methodology.
Patiño-Carachure, Cristóbal: contributed to the XRD and HRTEM characterization analyses.

Availability of data and materials

Data are available on request at: cpatino@pampano.unacar.mx

Abbreviations

XRD	X-Ray Diffraction
HRTEM	High Resolution Transmission Electron Microscopy
TEM	Transmission Electron Microscopy
MM	Mechanical Milling
HT	Heat Treatment

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Background

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Differences and discussions

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