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# **Structural study of functional hierarchical porous carbon synthesized from metal organic framework template**

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## **Abstract**

In this work, nitrogen-doped hierarchically porous carbon (NPC) was obtained from an effective and facile synthesis route based on MOF-drive approach using Zr-metal organic framework (UiO-66-NH<sub>2</sub>) as a template. The structural analysis of synthesized NPC employing different heat treatment was performed through X-ray diffraction (XRD), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and N<sub>2</sub> adsorption-desorption isotherm at 77K characterization. The results achieved indicate that Zr-MOF is an appropriate starting precursor to attain functional carbon materials with remarkable physicochemical properties for potential advanced applications. Thereby, it was evidenced that the NPC synthesis temperature has an influence on resulting structural properties as well as nitrogen functionalities and amount. Thereby, the obtained NPC exhibit a disorder porous structure with high BET surface area (765-867 m<sup>2</sup>/g), pore size from micro to mesoporous and 3-4% of N-content. Related to nitrogen functionalities, the heteroatom corresponds to quaternary, pyrrolic and pyridinic bonding indicating that it was successfully incorporated into the carbon framework.

**Keywords:** Metal-organic framework, template base synthesis, N-doped carbon, hierarchical porous carbon, physicochemical characterization.

## 1. Introduction

In the last years, carbon-based materials with desirable characteristic have received remarkable attention due to their growing demand in multiple areas. Particularly, heteroatom doped different carbon-based materials represent one of the most prominent materials used in many applications such as fuel cells, batteries and supercapacitor electrode or hydrogen storage [1]. The introduction of chemical functionality like heteroatoms (N, S, B, metals, etc.) into the carbon structures allows enhancing their physicochemical properties [2]. Particularly, nitrogen-doped carbon is a class of materials that contain small percentage of substitute nitrogen atoms which are present into carbon lattice in three common bonding configurations including quaternary N (or graphitic N), pyridinic N, and pyrrolic N. Among these nitrogen types, pyridinic N and pyrrolic N are related to two  $sp^2$  hybridized C atoms in the aromatic structure while the N quaternary is directly bonded with three tetrahedral  $sp^3$  hybridized carbon [3]. The pyrrolic N and pyridinic N usually show a planar platelet structure while quaternary N generally displays an uneven (three dimensional) structure [4]. Moreover, the N-functionalities distribution into carbon structures strongly depends on both the synthesis conditions and carbon and nitrogen precursors [5,6]. Theoretic calculations and experimental studies [7,8,9] have demonstrated that the carbon chemical doping effectively modifies their intrinsic properties including electronic characteristics, surface and local chemical features which provided advantages for advanced applications.

The nitrogen-doped carbon is conventionally synthesized via chemical-vapor-deposition (CVD), arc-discharge/vaporization or plasma treatment utilizing diverse nitrogen sources such as  $NH_3$  atmosphere, pyridine or acetonitrile as precursor [10].

However, this synthesis approach usually involves multistep procedures, rigorous reaction conditions with elevated energy consumption, and presents lowly control over N doping amount and state, chemical homogeneity, reproducibility and sometimes evidenced a carbon structure deterioration [10,11]. In this context, carbon research focuses on the synthesis of advanced carbon materials via template-based synthesis for better control of their physical and chemical properties as well as their morphology.

Recently, metalorganic frameworks (MOFs) resulting from the periodically arranged organometallic complexes in three-dimensional (3D) space have been demonstrated as a promising self-sacrificing template and precursors to produce porous carbons due to a large number of available structures, multiple functionalities, and versatile pore structures [12,13,14,15,16,17]. In this regard, the advantage of the MOFs templating base synthesis with or without additional functional medium is the procedure simplicity. Thereby, functional carbon materials with high porosity were successfully obtained from carbonization employed MOFs assembled from nitrogen-containing ligands, for instance, zeolitic imidazolate frameworks (ZIFs) [11,18,19,20,21,22,23,24,25,26] or isorecticular MOF (IRMOFs) [27] as starting precursors.

Previous studies [11,28,29] indicate that the inherent properties of the MOF template are the main factor responsible for the ordered pores formed in a carbon matrix. It was evidenced that MOF template with aromatic linkers, rigid architecture and high thermal stability allow it to retain the ordered morphology even after higher temperature carbonization [28]. Besides, the carbonization temperature is critical for structural evolution, thus the graphitization degree of carbon materials which improve the electronic conductivity can be induced at high-temperature treatment of MOFs [30]. Likewise, the nitrogen content and surface area are easily controlled by the

carbonization temperature. In this regard, high-temperature of carbonization enhances porosity; nevertheless, it causes considerable nitrogen functional loss [18,27].

Herein, a single-step pathway for the synthesis of nitrogen-doped highly porous carbon (NPC) materials containing graphitic frameworks is proposed. The functional NPC was synthesized from MOF-drive approach using alternative advanced porous Zirconium MOF containing 2-aminoterephthalic acid linker (UiO-66-NH<sub>2</sub>) as a template as well as a carbon and nitrogen source. The template was selected due to its intrinsic properties including an advanced structural arrangement with a regular nano-architecture, high surface area, well-defined pores, and nitrogen content. Additionally, the carbonization temperature effect on resulting NPC structural properties and doping level were evaluated. Furthermore, for structural analysis, the UiO-66-NH<sub>2</sub> template and synthesized functional porous carbon were characterized through XRD, TGA, SEM, TEM, N<sub>2</sub> adsorption-desorption isotherm, Raman spectroscopy, and XPS.

## **2. Materials and methods**

### **2.1. Synthesis of zirconium aminobenzenedicarboxylate MOF (UiO-66-NH<sub>2</sub>)**

The chemicals used in the UiO-66-NH<sub>2</sub> synthesis process were obtained from Sigma-Aldrich and include dimethylformamide (DMF, 99%), 2-amino-1,4-benzendicarboxylic acid (NH<sub>2</sub>-H<sub>2</sub>BDC 98.9%), benzoic acid (99%) and ZrCl<sub>4</sub> (99.9%). All chemical reagents were used without further purification.

The Zr-MOF was synthesized via solvothermal procedure using benzoic acid as a modulating agent [31]. Typically, 0.35 mmol ZrCl<sub>4</sub>, 4.0 mmol benzoic acid, and 0.35 mmol NH<sub>2</sub>-H<sub>2</sub>BDC were dissolved in DMF (20 ml), and the solution was heated in an autoclave at 120 °C for 24 h under static conditions. After that, the autoclave was

cooled to room temperature and the resulting solid was filtered, washed with DMF, and dried at room temperature under vacuum conditions.

## **2.2. Synthesis of nitrogen-doped porous carbon (NPC)**

The NPC materials were synthesized by direct carbonization of UIO-66-NH<sub>2</sub> template under nitrogen flow (20 mL min<sup>-1</sup>) at temperatures of 700 (NPC-700), 800 (NPC-800) and 900 °C (NPC-900) for 8h. The synthesis was carried out placing the organic template in a ceramic boat and the solid was pre-treated on nitrogen atmosphere at room temperature for 30 minutes. After that, the furnace was heated to corresponded carbonization temperature at 5 C°min<sup>-1</sup> rate. The resulting samples were washed with HF acid (30 %wt.) to remove the Zr component. Next, the solids were extensively washed with deionized water and dried at 100 °C.

## **2.3. Materials characterization**

The synthesized Zr-MOF template and NPC samples were structurally characterized by powder X-ray diffraction (Philips PW1710 diffractometer) using Cu K $\alpha$  radiation ( $\lambda=1.5406\text{\AA}$ ) operating at 45kV and 30mA. The XRD patterns were collected between 10 and 80° at 0.25°/min with a step size of 0.02°. Besides, the textural characterization was obtained from the N<sub>2</sub> adsorption-desorption isotherm at 77 K on ASAP 2000 Micromeritics instrument. Prior to measurement, the samples were evacuated 24 hours at 180 °C. The morphological analysis was examined by scanning electron microscopy (SEM) on a Carl Zeiss EVO MA10 instrument operating at 20 kV. Transmission Electron Microscopy (TEM) micrographs were taken on JEOL 100 CX II using 400 kV accelerating voltage. Moreover, the chemical composition was determined by elemental analysis (Exeter Analytical CE-440) and inductively coupled plasma

emission spectroscopy (ICP-ES) using a high-resolution Shimadzu 9000 multitype instrument.

The thermal stability of UiO-66-NH<sub>2</sub> template was evaluated by thermogravimetric analysis on a Discovery TGA analyzer (TA Instruments), with 1 °C min<sup>-1</sup> heating rate, from 25 to 800 °C under N<sub>2</sub> flow (25 mLmin<sup>-1</sup>).

Additionally, Raman spectra for synthesized carbon solids were measured using B&W Teki-Raman Plus (Newark, USA) spectrometer. Laser radiation was operated at a wavelength of 532 nm, with a spectral resolution of 4 cm<sup>-1</sup>, laser power of 10% and exposure time of 30 s. The chemical binding state and electronic structure of NPC solids were analyzed by X-ray photoelectron spectroscopy (XPS) in multi-technique system (SPECS) equipped with a hemispherical PHOIBOS 150 analyzer. The spectra were obtained using monochromatic Al K $\alpha$  radiation ( $h\nu = 1486.6$  eV) operated at 80 W. The pass energy for the scan element was 30 eV. The working pressure in the analyzing chamber was less than  $1.10^{-9}$  m bar.

### **3. Results and discussion**

The XRD profile (Fig. 1.a) of synthesized UiO-66-NH<sub>2</sub> presents all the reflections reported in the literature [33,32], indicating that the synthesized powder corresponds to the Zr-UIO-66 structure. The UiO-66-NH<sub>2</sub> containing 2-aminoterephthalic acid linker has a face-centered cubic crystal structure and Zr<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub>(C<sub>2</sub>O<sub>4</sub>-NH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)<sub>6</sub> empirical formula. The MOF template framework consists of Zr<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub> clusters interconnected with twelve NH<sub>2</sub>-BDC linkers to form the 3D structure based on tetrahedral and octahedral cages [33,34].

Furthermore, the thermal stability and structural integrity at elevated temperatures of the Zr-MOF template were examined by thermogravimetric analysis. The TGA



profile (Fig. 1.b) exhibits two weight loss stages. The first weight loss (~31%) with a clear step close to 100°C followed by the progressive weight loss up to 330°C corresponds to the removal of physisorbed water molecules and residual solvent occlude inside the porous. The second stage in 330-500 °C interval (~38 %) is attributed to subsequent structure amorphization and pore collapse, which is in accordance with literature result [34]. Moreover, taking into account that after thermal treatment the final product is ZrO<sub>2</sub>, the corresponding weight loss of ZrO(CO<sub>2</sub>)<sub>2</sub>(NH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>) ideal dehydrated and desolvated framework relative to the last step is expected to be near ~57.1 %. However, the synthesized UiO-66-NH<sub>2</sub> structure evidences a relative weight loss of ~55.1 %, suggesting that the obtained material presents a slight structural defect undetected by crystallographic methods.

In addition, the chemical composition of the synthesized UiO-66-NH<sub>2</sub> was inferred from ICP-ES and elemental analysis. The results obtained (Table 1) present a marginal difference in organic ligand to Zr ratio regarding the stoichiometrically framework, which represents low defect content (3.3 %) and a coordination number of 11.6. This structural defect is related to the random absence of some NH<sub>2</sub>-BDC linkers in the framework. Wu et al. [35] evidenced that the acetic acid modulating agent in Zr-MOF synthesis provides the intermediary reactants to regulate the MOF crystal growth and it participates in linker vacancies formation. Nevertheless, the mechanism of how acetic acid affects the morphology and induces the missing-linker defects in the sample is not clear yet.

The template porous structure of outgassed Zr-UiO-66-NH<sub>2</sub> was analyzed by N<sub>2</sub> adsorption (Fig. 1.c) and the textural parameters are summarized in Table 2. The solid exhibit a type-I N<sub>2</sub> physisorption isotherm with a significant N<sub>2</sub> uptake at low relative pressures ( $P/P_0=0.02$ ), well-defined knees and plateaus typical of microporous

materials. A previous report [35] has demonstrated that the UiO-66 MOF structural defect relative to linkers vacancies increases significantly the porosity. Nevertheless, the textural properties of Zr-MOF template obtained in this work were close to the  $954 \text{ m}^2\text{g}^{-1}$  and  $0.43 \text{ cm}^3\text{g}^{-1}$  theoretical values reported for ideal UiO-66 crystal [35]. This result confirms that the structural defects induced for the benzoic acid modulating agent are very low.

The morphologies of Zr-MOF templating crystal were characterized by TEM (Fig. 1 d.) and SEM (Fig. 1.e) micrography. The TEM image reveals a highly monodispersed and uniformly distributed regular microcrystals. SEM images of UiO-66-NH<sub>2</sub> demonstrated a successful preparation. Thus, the Zr-MOF particles exhibit the typical regular intergrown octahedral nanocrystals with particle size about 80-200.

**Figure 1.**

**Table 1.**

**Table 2.**

The XRD pattern of NPC-700, NPC-800 and NPC-900 samples (Fig. 2) obtained after MOF template carbonization display similar features with a broad peak at approximately  $25^\circ$  and a low-intensity signal at  $44^\circ$  corresponding to (002) and (100) diffraction planes of graphitic layers, respectively. In this regard, the broad (002) reflections indicate the presences of small domains of graphitic sheets parallel stacking, while the (100) reflections correspond to honeycomb structures originated from  $sp^2$  hybridized carbons [36]. **In addition, the values of spacing carbon layer ( $d_{002}$ ) and basic**

structural unit size along the c-axis ( $L_c$ ) estimated from Bragg law and Debye-Scherrer equation, respectively, are presented in Table 3. It was observed, that the  $d_{002}$  values are between 3.53 and 3.63 Å which are larger than the interlayer spacing of 3.335 Å for ideal graphite crystal indicating many defects and disordered structures. The NPC samples show small values of basic structural unit size along the c-axis ( $L_c$ ) indicating a limited level of crystalline development which can be attributed either the low layer planes alignment or hollow presence [37]. In addition, the obtained results evidenced that a calcination temperature increase produces a slight intensity enhance due to structural changes which involve a graphitization degree improvement. Moreover, it is important to highlight that no additional signals of impurities such as Zr or  $ZrO_2$  were observed on XRD profile indicating that the after-HF treatment the zirconium was removed, and final products correspond to metal-free carbons.

### **Figure 2.**

The textural characterization of the NPC solids synthesized from Zr-MOF template was analyzed by  $N_2$  physisorption and the textural properties are summarized in Table 2. The samples  $N_2$  adsorption-desorption isotherm shape (Fig. 3.a) show a fast increase of adsorbed volume at low relative pressure area ( $P/P_0 < 0.1$ ) reflecting the abundant micropores existence, followed by a plateau region and a steep rise at high relative pressure ( $P/P_0 > 0.9$ ). The almost vertical tails at elevated relative pressure assigned to macropores presences probably originated from interstitial voids between the resulting particle [18]. Additionally, the NPC-900 solid displays a clear hysteresis between adsorption-desorption branches at medium relative pressure which demonstrates the large mesoporous existence. The pore size distributions calculated by

Non-Local Density Functional Theory (NLDFT) method using adsorption branches are given in Fig. 3.b-c. The pore size distributions display that all the synthesized samples present a well-defined microporous structure inherited from the microporous Zr-MOF precursor and mesoporosity resulting from the intrinsic carbon structure and defects. Therefore, the resulting NPC shows that the UIO-66-NH<sub>2</sub> micropores were preserved (Fig. 1.d).

Furthermore, the NPC samples porosity characteristic are in good agreement with those of the initial Zr-MOF precursor. Nevertheless, the BET surface area and micropores pore volume reduction of resulting NPC could be attributed to the starting template structure shrinkage due to the nanoporous architecture collapse and subsequent graphitization. The NPC-700 and NPC-800 solids show similar behavior with slight enhancement of BET and micropores surface area indicating that the calcination temperature increasing from 700 °C to 800 °C does not produce significant changes of textural properties (Table 2). However, the NPC-900 solid presents quite different pore properties relative to the NPC-700 and NPC-800 samples. The high carbonization temperature (900 °C) leads to highest meso-, total pore volume, and surface area. These results evidencing that the synthesis temperature increase influences on the framework template decomposition, which involves two stages. At high temperature, the framework primary crystals disassembly takes place, and subsequently, the ligand decomposition with nitrogen and carbon evolution is produced to generate a porous carbon network [38].

**Figure 3.**

Raman spectroscopy was performed to investigate the bonding structure of synthesized N-doped carbon. The Raman spectra of samples (Fig. 4.a) display two main overlapping bands with maximal intensity at about  $1360\text{ cm}^{-1}$  (D1) and  $1580\text{ cm}^{-1}$  (G) which correspond to  $E_{2g}$  and  $A_{1g}$  vibrational modes, respectively. Thereby, the G band belongs to ideal graphitic lattice and the D1 band is correlated with disordered carbon or defective graphitic structure which includes a large family of  $sp^2$  carbon bond [39,40]. Moreover, the second-order spectral region between  $2500$  and  $3500\text{ cm}^{-1}$  show broad and less intense bands assigned to D bands overtone (2D) characteristic features of graphitic layers and combination modes [40].

In order to derive structural information, the first-order bands ( $800\text{-}2000\text{ cm}^{-1}$ ) were decomposed into five components (Figure 4.d-c) G ( $1580\text{ cm}^{-1}$ ), D1 ( $1360\text{ cm}^{-1}$ ), D2 ( $\sim 1610\text{ cm}^{-1}$ ), D3 ( $\sim 1480\text{ cm}^{-1}$ ) and D4 ( $\sim 1250\text{ cm}^{-1}$ ) using Lorentzian and Gaussian functions according to Sadezky et al. [41] method. In general, the three additional bands (D2, D3, and D4) are attributed to edge effect, plane defects, heteroatoms or double bonds presence and amorphous structure [41,42]. The presence of D peaks in the carbon synthesized at different calcination temperatures indicates that the graphitic phase was not developed. However, the different height and area distribution of typical carbon bands among the samples allow inferring structural differences with the synthesis temperature. In addition, based on the relative intensity ratio values ( $I_{D1}/I_G$ ) (Table 3) obtained by spectra fitting, it was confirmed that the solid studied presents highly disorder-defect structure which could be attributed to both nitrogen and oxygen content and edge effect [43]. Likewise, the  $I_{D1}/I_G$ ,  $A_{D1}/A_G$  parameters decrease as the calcination temperature enhances, demonstrating that the synthesis temperature reduces the amount of structural defect since it reduces the N-doping concentration and contributes with the graphitic  $sp^2$  carbon formation.

#### **Figure 4.**

#### **Table 3.**

Additionally, to check the samples compositions and N-doping amount of NPC solids, the elemental analysis was performed. The results confirm that the main composition was carbon (Table 4) with nitrogen amounts between 3 and 4 wt%. Also, the detected oxygen (~21-25 wt%) and hydrogen (~0.9-1.4 wt%) are related to the oxygen-containing carbon network, hydroxyl groups, and adsorbed water molecules. Besides, the ICP-ES results validate the absence of traceable Zr species in the NPC samples.

In order to understand the N-functionalities introduced in the carbon structure, X-ray photoelectron spectroscopy (XPS) was performed. The spectra for synthesized NPC samples (Fig. 5) evidence three major signals centered at binding energy values of 285.2, 532.5 and 400.2 eV which are consistent with C 1s, O 1s, and N 1s presence, respectively. Table 4 summarized the elemental composition for NPC solids. The results are in good agreement with elemental analysis trend and notice that the N doped concentration decreased from 2.9 to 1.9 % with the calcination temperature increase from 700 to 900°C. This trend is assigned to the fact that C-C bonding (370 kJ/mol) is more favorable than C-N bonding (305 kJ/mol) at high growth temperatures [44]. On the other hand, it is possible that the stable N<sub>2</sub> molecules are generated and released as the temperature increases [45].

Moreover, to recognize the bonding environment, the C1s spectra region is deconvoluted into four peaks as shown in Fig. 6.b-d. Likewise, the signal at 285.2 eV binding energy is related to sp<sup>2</sup> C-C (C1), as well, the 286.6 (C2) and 287.5 (C3) eV

peaks corresponding to the N-sp<sup>2</sup> C and N-sp<sup>3</sup> C bonding structures, respectively. Also, the signal at 289.2 eV binding energy is attributed to CO- bond originated from surface oxygen absorption [46,47]. According to the XPS measurements, sp<sup>2</sup> C-C is the major surface carbon functional component (Table 5) indicating that the most carbon atoms for synthesized NPC samples are arranged in a conjugated honeycomb lattice. On the other hand, C2 and C3 signals confirm the nitrogen bonded presence into the carbon framework. In addition, the N1s band was deconvoluted into three peaks (Figure 5.e-g) located at 398.6, 400.2 and 401.0 eV which are assigned to pyridinic (N6), pyrrolic or pyridone (N5) and quaternary (NQ) nitrogen, respectively [4,5]. According to the literature [48,49], N5 and N6 signals denote N atoms located in a  $\pi$  conjugated system and contribute to the  $\pi$  system with one and two p-electrons, respectively. Furthermore, the NQ refers to the highly coordinated N atoms substituting sp<sup>2</sup> C in graphitic structures. Concerning relative concentration of N functionalities (Table 5) resulting from fitting procedures, N5 and NQ are the major contributions followed by N-6, which indicates that the N doping was successfully incorporated into the carbon framework. Nevertheless, as the calcination temperature increases, a reduction of atomic content of N5 and N6 with the concomitant increase of NQ functionalities was observed. This fact is attributed to the easy transformation from less stable N5 species via N6 forms to N-Q accompanied by nitrogen partly release [5,50]. Pels et al. [5] indicated that the conversion of N5 into N6 involves the transformation of pyridone-N (N5) to pyridinic-N (N6) attributable to oxygen loss and the pyrrolic-N (N5) ring expansion to generate pyridinic-N (N6) functionality. Moreover, N6 changes into N-Q through condensation reactions.

**Figure 5.**

#### **Table 4.**

#### **Table 5.**

The SEM images of NPC solids synthesized at different calcination temperatures (Fig. 6) evidence that the samples have similar morphologies composed of polyhedron particles. The samples particles size is between 80 and 180 nm for NPC-700, 80 and 260 nm for NPC-800 and 80-200 nm for NPC-900, which displays that the carbons particle size distribution does not appreciably change with the carbonization temperature increase. In addition, the TEM micrographs (Fig. 7) demonstrate nanovoids distributed over a particle area which increases with the calcination temperature in good agreement with N<sub>2</sub> physisorption results. Furthermore, from SEM and TEM images evidenced that the functional carbon samples have similar shapes and surface structures than the original UiO-66-NH<sub>2</sub> template after calcination from 700°C to 900°C, indicating that the structural arrangement of MOF is the main responsible factor for the formation of the ordered pores in the carbon matrix.

#### **Figure 6.**

#### **Figure7.**

#### **4. Conclusion**

In summary, N-doped hierarchical porous carbon was synthesized from carbonization process employing Zr-MOF containing NH<sub>2</sub> functional group (UiO-66-



NH<sub>2</sub>) as both sacrificial template and carbon and nitrogen source. In this regard, the carbonization process was performed at different temperatures between 700 and 900°C without addition of a secondary carbon source. The results achieved demonstrate that the synthesis temperature (700-800 °C), has an influence on the resulting NPC structural properties as well as nitrogen functionalities and amount. In this concern, it was evidenced that the surface areas and pore volumes increase from 765.3 to 866.8 m<sup>2</sup>g<sup>-1</sup> and 0.52 to 0.68 cm<sup>3</sup>g<sup>-1</sup>, respectively, while the N contents show the opposite trends decreasing from 4.0 to 3.0% as the temperature increases. Related to N doping bonding, the heteroatom is present predominantly in quaternary, pyrrolic and pyridinic functionalities indicating that the N was successfully incorporated into the carbon framework.

Thereby, in this study, it was evidenced that the Zr-MOF starting precursor and controlled templated carbonization generate an efficient approach to attain a rational design of functional porous carbon with remarkable physicochemical properties. The NPC structures and functional properties achieved are attractive for potential advanced applications, mainly as promising active materials for energy-related utilization including fuel-cells, supercapacitors, and batteries technologies.

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